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MATHEMATICS

ON THE MOMENT PROBLEM FOR A FINITE INTERVAL

By L. KANTOROVIČ

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In this paper, some theorems (partly new and partly already known) are proved, concerning the problem of moments for the interval (0,1). The proofs of these theorems are based on the properties of Bernstein's polynomials and on some general conceptions of the functional analysis.

We shall introduce the following notations. Let

$$\mu^{(0)},\ \mu^{(1)},\ \ldots \tag{1}$$

be a system of numbers. If $P(x)$ is a polynomial: $P(x) = \sum_{k=0}^{m} a_k x^k$, we denote $P(\mu) = \sum_{k=0}^{m} a_k \mu^{(k)}$. We shall write also $P \geqslant 0$, if for any $x \in (0,1)$ we have $P(x) \geqslant 0$.

§ 1. Theorem 1 [of Hausdorff (1)]. In order that in the interval (0, 1) a non-decreasing function $g(x)$ existed such that

$$\int_0^1 x^k dg(x) = \mu^{(k)}, \qquad (k = 0,\ 1,\ 2,\ \ldots) \tag{2}$$

it is necessary and sufficient, that for any k and m the following inequality should hold

$$\Delta^m \mu^{(k)} = (1-\mu)^m \mu^{(k)} = \sum_{i=0}^{m} C_m^i (-1)^i \mu^{(k+i)} \geqslant 0. \tag{3}$$

Proof. (A) Necessity. If the non-decreasing function $g(x)$ satisiying our conditions does exist, then for any $P \geqslant 0$, we have

$$P(\mu) = \int_0^1 P(x)\, dg(x) \geqslant 0$$

Setting here $(1-x)^m x^k$ instead of $P(x)$, we obtain at once the condition (3).

(B) Sufficiency. Let $P(x)$ be a polynomial of s-th degree. Let us write down its polynomial of Bernstein

$$B_n(P;\ x) = \sum_{k=0}^{n} C_n^k x^k (1-x)^{n-k} P\left(\frac{k}{n}\right). \tag{4}$$

If we know that $P \geqslant 0$, then the expression (4) for $B_n(P; x)$ and the condition (3) will give us immediately

$$B_n(P;\ \mu) = \sum_{k=0}^{n} C_n^k \mu^{(k)} (1-\mu)^{n-k} P\left(\frac{k}{n}\right) \geqslant 0.$$

The polynomials $B_n(P; x)$ are of not more than s-th degree and converge uniformly towards $P(x)$; consequently, their coefficients converge respectively to the coefficients of P, and therefore $\lim B_n(P;\ \mu) = P(\mu)$, whence $P(\mu) \geqslant 0$.

If now $P \geqslant 0$ and if we denote $\| P \| = \max\limits_{0 \leqslant x \leqslant 1} P\ (x)$, we have (because $0 \leqslant P(x) \leqslant \| P \|$)

$$0 \leqslant P(\mu) \leqslant \| P \| \cdot \mu^{(0)}. \tag{5}$$

Let now $f(x)$ be an arbitrary function continuous in the interval $(0, 1)$. Then, owing to the unequality (5), a limit

$$\lim_{n \to \infty} B_n(f;\ \mu) = G(f)$$

exists. Evidently, $G(f)$ is a positive linear functional in the space of continuous function ($G(f) \geqslant 0$ if $f \geqslant 0$). Consequently, it may be represented as follows

$$G(f) = \int_0^1 f(x)\, dg(x), \tag{6}$$

where $g(x)$ is an increasing function $\big(g(0) = 0\big)$. This function $g(x)$ will evidently satisfy the relations (2). Hence, the theorem is proved.

In this paragraph we used partly the considerations of Hildebrandt and Schoenberg (2).

§ 2. If the conditions (3) are satisfied for the sequence $\mu^{(0)}$, $\mu^{(1)}$, $\mu^{(2)}$, ..., we can determine effectively the function $g(x)$. In fact, denote $\varkappa(x, y)$ the function of x and y which is equal to 1 when $y \leqslant x$ and to 0 when $y > x$. Then, at any rate at the points of continuity of $g(x)$, we shall have $g(x) = \int_0^1 \varkappa(x, y)\, dg(y)$. Take the polynomials

$$\pi_n(x, y) = \sum_{i,\ k=0}^{n} a_{i,\ k}^{(n)} x^i y^k,$$

which decreasing converge towards $\varkappa(x, y)$ [e. g., we can take for $\pi_n(x, y)$ the n-th polynomial of Bernstein for the function $\frac{1}{n} + \varkappa\left(x + n^{-\frac{1}{3}},\ y\right)$].

Setting now

$$g_n(x) = \int_0^1 \tau_n(x,\ y)\, dg(y) = \sum_{i,\ k=0}^{n} \alpha_{i,\ k}^{(n)} \mu^{(k)} x^i,$$

we obtain a sequence of polynomials which decreasing converge towards $g(x)$ [if x is a point of discontinuity of $g(x)$, then they converge towards $g(x+0)$].

In a similar manner, increasing sequence of polynomials converging towards $g(x)$ may be constructed.

§ 3. It is interesting to find out what conditions should satisfy the moments $\mu^{(0)}$, $\mu^{(1)}$, ... in order that the function $g(x)$ might belong to other classes. We shall give here two theorems giving the solutions of this problem for two particular classes.

Theorem 2. In order that a function $g(x)$ existed satisfying the relations (2) and the condition of Lipschitz $|g(x_2) - g(x_1)| \leqslant C|x_2 - x_1|$ for any x_1, x_2, where C is a constant, it is necessary and sufficient that

$$|\Delta^m \mu^{(k)}| \leqslant C \cdot B(m+1,\ k+1). \tag{7}$$

Proof. (A) Necessity.

$$|\Delta^m \mu^{(k)}| = \left| \int_0^1 x^k (1-x)^m g'(x)\, dx \right| \leqslant C\, B(m+1,\ k+1).$$

(B) Sufficiency. Let the inequality (7) hold for the $\mu^{(k)}$'s; then, setting $\bar{\mu}^{(k)} = \mu^{(k)} + \frac{C}{k+1}$, we obtain a sequence satisfying the condition (3).

The numbers $\bar{\mu}^{(0)}$, $\bar{\mu}^{(1)}$, ... will be then the moments for a monotonic function $\bar{g}(x)$. Setting $g(x) = \bar{g}(x) - Cx$, we obtain a function satisfying the relations (3) and the condition of Lipschitz.

Theorem 3. In order that a monotonic function $g(x)$ of the class A^p $(p > 1)$ (i. e. a function which is an indefinite integral of a function integrable in Lebesgue's sense together with its p-th power) existed satisfying the conditions (3), it is necessary and sufficient that for every m and k

$$0 \leqslant \Delta^m \mu^{(k)} \leqslant H \left\{ B(kp'+1,\ mp'+1) \right\}^{\frac{1}{p'}}. \qquad \left(\frac{1}{p'} + \frac{1}{p} = 1 \right) \tag{8}$$

Proof. (A) Necessity

$$0 \leqslant \Delta^m \mu^{(k)} \leqslant \int_0^1 x^k (1-x)^m g'(x)\, dx \leqslant$$

$$\leqslant \left\{ \int_0^1 x^{kp'} (1-x)^{mp'} dx \right\}^{\frac{1}{p'}} \left\{ \int_0^1 [g'(x)]^p\, dx \right\}^{\frac{1}{p}} =$$

$$= H \left\{ B(kp'+1,\ mp'+1) \right\}^{\frac{1}{p'}}.$$

(B) Sufficiency. The condition $\Delta^m \mu^{(k)} \geqslant 0$ ensures the existence of a monotonic function $g(x)$ satisfying the relations (2).

For every continuous (and even for every bounded) function f, the functional $G(f)$ can be defined.

As soon as we establish the inequality

$$|G(f)| \leqslant H_1 \left\{ \int_0^1 |f'(x)|^{p'} dx \right\}^{\frac{1}{p'}}, \tag{9}$$

our theorem will be proved, because then the functional $G(f)$ may be extended over the space $L^{p'}$ and, consequently, the function $g(x)$ must belong to the class A^p.

Denote now $\varphi_{c,\,d}(x)$ the characteristic function of the interval $(c,\ d)$ and let us begin with the case when the interval $(c,\ d)$ is a small interval of the type $\left(\frac{k}{n} - \frac{1}{nh},\ \frac{k}{n} + \frac{1}{nh}\right)$, where $h = \sqrt{\frac{n}{2k(n-k)}}$ and $\frac{k}{n}$ is far from 0 and 1. Consider the polynomial $\chi(x) = \frac{e\sqrt{\pi}}{h} C_n^k x^k (1-x)^{n-k}$. Then, $\chi(x)$ being near to $e^{1-(nh)^2\left(x-\frac{k}{n}\right)^2}$, we have $\chi(x) \geqslant 1$ in $(c,\ d)$ whence $G(\varphi_{c,\,d}) \leqslant G(\chi)$. Now, because of the condition (8), the inequality (9) is true for $f = \chi$ and $H_1 = H$.

It is easily seen also that

$$\left\{ \int_0^1 |\chi(x)|^{p'} dx \right\}^{\frac{1}{p'}} \leqslant A_{p'} \left\{ \int_0^1 |\varphi_{c,\,d}(x)|^{p'} dx \right\}^{\frac{1}{p'}},$$

where $A_{p'}$ is a constant. Comparing all these inequalities, we obtain the inequality (9) for $f = \varphi_{c,\,d}$ and $H_1 = A_{p'} \cdot H + \varepsilon$, where ε is arbitrarily small for a sufficiently small interval $(c,\ d)$. Now the arbitrary interval may be expressed as a disjunctive sum of intervals of the type considered. Consequently, the inequality (9) holds for $f = \varphi_{c,\,d}$, where $(c,\ d)$ is an arbitrary interval, and $H_1 = A_{p'} \cdot H$.

But hence clearly follows that the same inequality with the same value of H_1 is true for any function $\varphi_{c,\,d}$ (because when the characteristic functions of disjunctive intervals are added, we have

$$\int_0^1 \left| \sum_k \varphi_{c_k,\ d_k}(x) \right|^{p'} dx = \sum_k \int_0^1 |\varphi_{c_k,\ d_k}(x)|^{p'} dx \Big).$$

And hence follows that the inequality (9) holds for any bounded function.

It should be noted that other (more complicated) solutions of the problems treated in Theorems 2 and 3 may be found in the works of Boas ([3]).

§ 4. Let M be the space of bounded functions $f(x)$ (defined on the segment $(0,\ 1)$ with the norm defined by the formula $\|f\| = \sup_{0 \leqslant x \leqslant 1} |f(x)|$). A subset E of M we shall call linear if, together with any two functions f_1 and f_2, it contains also the function $\lambda_1 f_1 + \lambda_2 f_2$. An additive functional $G(f)$ defined upon E we shall call positive (on E) if $G(f) \geqslant 0$ whenever $f \geqslant 0$. We shall prove now the following lemma.

Lemma. Let $E_0 \subset M$ be a linear set containing 1 (i. e. the function $f(x) \equiv 1$), and G be a positive functional defined on E_0. Then the functional G can be extended over M so as to remain positive.

Proof. Let f^* be an element of M not belonging to E_0. Denote

$$m = \sup_{f_1 < f^*} G(f_1); \quad M = \inf_{f_2 > f^*} G(f_2). \qquad (f_1, f_2, \in E_0)$$

The numbers m and M are finite, because the functions identically equal to $-\|f^*\|$ and $\|f^*\|$ resp. belong to E_0 and $-\|f^*\| < f < \|f^*\|$. Besides, if $f_1 \leqslant f^* \leqslant f_2$, we have ($G$ being positive) $G(f_1) \leqslant G(f_2)$. This proves that $m \leqslant M$.

Let μ be an arbitrary number such that $m \leqslant \mu \leqslant M$. Denote E_1 the set of all the elements of M of the form $f = f_0 + \alpha f^*$, where $f_0 \in E_0$ and α is a real number. We shall define the functional $G(f)$ on E_1 as follows

$$G_1(f) = G(f_0) + \alpha\mu.$$

Thus: 1) G_1 is univocally determined (because no function can have more than one representation of the form $f_0 + \alpha f^*$, $f_0 \in E_0$; 2) if $f \in E_0$, we have $G_1(f) = G(f)$; 3) G_1 is positive. In fact, let $f \in E_1$, $f \geqslant 0$. Represent f in the form $f = f_0 + \alpha f^*$ and let, for instance, $\alpha > 0$. Then $-\frac{1}{\alpha} f_0 < f^*$, hence $-\frac{1}{\alpha} G(f_0) \leqslant m \leqslant \mu$, and therefore $G_1(f) = G(f_0) + \alpha\mu \geqslant 0$. For the case when $\alpha < 0$, the reasoning is the same.

Joining now a new function f^{**} non $\in E_1$, we obtain E_2 and G_2 defined over E_2 and so on in a transfinite induction [comp. the similar reasoning in the proof of Hahn-Banach's theorem (4)] until we obtain the whole space M. Thus the lemma is proved.

Theorem 4. Let a finite or infinite number of the elements of the space C of continuous functions

$$f_0 = 1, \ f_1, \ f_2, \ \ldots$$

be given, as well as the same number of real numbers $\mu^{(0)}, \mu^{(1)}, \mu^{(2)}, \ldots$ Then, in order that a positive functional G [and consequently a corresponding monotonic function $g(x)$ defined in $(0, 1)$] existed satisfying the conditions

$$G(f_i) = \int_0^1 f_i(x)\, dg(x) = \mu^{(i)}, \qquad (i = 0, \ 1, \ 2, \ \ldots)$$

it is necessary and sufficient that for any system of real numbers $\alpha_0, \alpha_1, \ldots, \alpha_n$ the inequality $\sum_{i=0}^{n} \alpha_i f_i \geqslant 0$ involved the inequality $\sum_{i=0}^{n} \alpha_i \mu^{(i)} \geqslant 0$.

Proof. (A) Necessity. If the functional G satisfying the conditions of the theorem exists, then the inequality $\sum_{i=0}^{n} \alpha_i f_i \geqslant 0$ implies

$$G\left(\sum_{i=0}^{n} \alpha_i f_i\right) \geqslant 0, \text{ i. e. } \sum_{i=0}^{n} \alpha_i G(f_i) = \sum_{i=0}^{n} \alpha_i \mu^{(i)} \geqslant 0.$$

(B) Sufficiency. Denote E_0 the set of all the elements of the

form $f = \sum_{i=0}^{n} \alpha_i f_i$ $(n = 1, 2, \ldots)$ and $G(f) = \sum_{i=0}^{n} \alpha_i f_i$ (it may be easily seen that $G(f)$ is univocaly determined for every $f \in E_0$). Then all the premises of the preceding lemma are satisfied and its conclusion is therefore true, i. e. a positive functional $G'(f)$ defined in M (and therefore in C) exists coinciding with G on E_0. This functional can be represented by the integral of Stiltjes $G'(f) = \int_0^1 f(x)\, dg(x)$, where $g(x)$ is a non-decreasing function. The theorem is thus proved.

§ 5. As an application of Theorem 4, we propose to prove the theorem of Krein and Achyeser (5) on the continuation of a sequence of moments. The problem of the continuation of moments was proposed by A. Markoff (6).

Theorem 5. Let the numbers $\mu^{(0)}, \mu^{(1)}, \ldots, \mu^{(n)}$ be given. In order that a monotonic non-decreasing function $g(x)$ existed, satisfying the conditions

$$\int_0^1 x^\nu\, dg(x) = \mu^{(\nu)}, \qquad (\nu = 0, 1, \ldots, m) \tag{10}$$

it is necessary and sufficient that the following quadratic forms were positive:

$$\sum_{i,\,j=0}^{k} \mu^{(i+j+1)} a_i a_j; \quad \sum_{i,\,j=0}^{k} (\mu^{(i+j)}\mu^{(i+j+1)})\, a_i a_j; \quad \text{when } m = 2k+1;$$

$$\sum_{i,\,j=0}^{k} \mu^{(i+j)} a_i a_j; \quad \sum_{i,\,j=0}^{k-1} (\mu^{(i+j+1)}\mu^{(i+j+2)})\, a_i a_j; \quad \text{when } m = 2k.$$

Proof. Let $P(x) = \sum_{i=0}^{m} h_i x^i$. Let $H^2(P) = \sum_{i=0}^{m} h_i \mu^{(i)}$. It is evidently that among the polynomials $P(x) \geqslant 0$ satisfying the condition $H(P) = 1$ there in $(0,1)$ exists such a one for which the value of $P(\mu) = \sum_{i=0}^{m} h_i \mu^{(i)}$ attains its minimum. Denote such a polynomial $P_0(x)$. We say that all m roots of $P_0(x)$ lie in the segment $(0,1)$. In fact, let $\xi_1, \xi_2, \ldots, \xi_j (j \leqslant m)$ be all the roots of P_0 lying in $(0,1)$ and denote $\pi(x) = A(x - \xi_1) \ldots (x - \xi_j)$, where the constant A is so chosen that $H(\pi) = 1$ (if $j = 0$, then $\pi(x) = 1$). If we set now $P_1(x) = \big(P_0(x) + \lambda\pi(x)\big) H^{-1}(P_0 + \lambda\pi)$, then, for $|\lambda|$ sufficiently small, we shall have $P_1(x) \geqslant 0$ in $(0,1)$. On the other hand.

$$P_1(\mu) = \frac{P_0(\mu) + \lambda\pi(\mu)}{H(P_0 + \lambda\pi)} = \frac{P_0(\mu) + \lambda\pi(\mu)}{\sqrt{1 + \lambda\big(H^2(P_0 + \Pi) - 2\big) + \lambda^2}}.$$

As for the polynomial P_0 the expression $P_1(\mu)$ attains its minimum, we must have $P_1(\mu) \geqslant P_0(\mu)$ for any λ, which is possible only if $\pi(\mu) = \pm P_0(\mu)$ and $H^2(P_0 + \Pi) - 2 = \pm 2$. But the last condition means that $P_0(x) = \pm\pi(x)$, and thus the fact that all the roots of $P_0(x)$ lie on

the segment $(0, 1)$ is established. Now, $P_0(x)$ being non-negative on the segment $(0, 1)$, all its roots, except perhaps those at the end points of $(0,1)$ are of an even order, and we can write $P_0(x)$ in one of the forms:

$$xR_k^2(x) \text{ or } (1-x)R_k^2(x) \text{ if } m = 2\kappa + 1;$$
$$R_k^2(x) \text{ or } (x-x^2)R_{k-1}^2(x); \text{ if } m = 2k,$$

where $R_k(x)$ and $R_{k-1}(x)$ are polynomials of the order k resp. $k-1$.

Let, e. g., $P_0(x) = xR_k^2(x)$; then

$$P_0(\mu) = \mu\Big(\sum_{i=0}^{k} a_i \mu^{(i)}\Big)^2 = \sum_{i,\ j=0}^{k} \mu^{(i+j+1)} a_i a_k \geqslant 0$$

by the condition of the theorem. The other cases will be treated analogically. As $P_0(\mu) \geqslant 0$, we have $P(\mu) \geqslant 0$ for every polynomial $P \geqslant 0$. Applying now theorem 4 (for $f_i(x) = x^i$, $i = 0, 1, 2, \ldots, m$), we prove the existence of the function $g(x)$ satisfying (10).

Remark. If we want the function $g(x)$ in Theorem 5 to satisfy the supplementary condition $g(x_2) - g(x_1) \leqslant C(x_2 - x_1)$, then we must ask in the premise of Theorem 5 that the above-mentioned quadratic forms remain positive if we substitute $\frac{C}{k+1} - \mu^{(i)}$ for $\mu^{(i)}$. This can be proved by the same reasonings as in Theorem 2.

Another solution of this problem was proposed by Krein and Achyeser (7).

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II

SOME THEOREMS ON THE ALMOST EVERYWHERE CONVERGENCE

By L. KANTOROVIČ

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In my recent paper «On Sequences of Linear Operations» (1) some theorems were given on the convergence of the sequences of linear operations in a semi-ordered space. Here I propose to apply these theorems chiefly to the case when Y (see the above-cited paper) is the space S of the measurable functions. As the (o)-convergence is, in this case, the almost everywhere convergence (2), we have thus a general method for establishing a number of theorems, on the almost everywhere convergence, partly new and partly already known and proved by other methods.

§ 1. Theorem. Let X be a regular semi-ordered space or a linear metric space, $U_n(x)$—a sequence of linear operations of the class H_1' transforming X into the space S of measurable functions, i. e.

$$y(t) = U_n(x, t).$$

Suppose that the following conditions are satisfied: 1) For every $x \in X$ $\overline{\lim_{n\to\infty}} U_n(x, t)$ is finite for almost all values of t. 2) For every x belonging to a certain set everywhere dense in X, $\lim_{n\to\infty} U_n(x, t)$ exists for almost all values of t. Then the sequence $U_n(x, t)$ converges for almost all values of t for every $x \in X$.

Proof. Substituting in the first condition —x, for x, we see that $\lim_{n\to\infty} U_n(x, t)$ is also finite for almost all values of t. Hence, for every $x \in X$ the set of functions $\{ U_n(x, t) \}$ is bounded in S. We can therefore apply the theorem 6 of my paper [1] and thus arrive at the conclusion of the theorem. For the case when X is a normed space this theorem has been established by S. Banach [3].

§ 2. Let $x(t)$ be a function defined upon an interval (a, b) und integrable (in Lebesgue's sense) upon this interval. Let further I be a mobile interval situated near the point s, and $|I|$ its length. We shall now consider the question of the convergence towards $x(s)$ of differential quotients of the primitive function (integral) for the function $x(t)$:

$$U_I(x, s) = \frac{1}{|I|} \int_I x(t)\, dt$$

as $|I| \to 0$.

These differential quotients are linear operations and will be considered as such.

If we put

$$x^*(s) = \sup_I U_I(x, s),$$

then, as Hardy and Littlewood have shown [4], if $x \in L^p$, the function x^* also belongs to L^p. Consequently, if we consider the operations $U_I(x)$ as operations transforming L^p into L^p, the set of their values is for every x (o)-bounded. It is evident, besides, that for continuous functions $x(t)$ (which constitute a set everywhere dense in L^p), the functions $U_I(x, s)$ converge uniformly towards $x(s)$.

Applying now Theorem 6 of the paper cited [1], we obtain the following result:

If a function $x(t)$ is of the class L^p, then the differential quotients of its primitive function (o)-converge towards $x(s)$ in the space L^p.

In a similar way, we can prove that if

$$\int_a^b |x(t)| \lg^+ |x(t)|\, dt < +\infty$$

then these differential quotients (o)-converge towards $x(s)$ in the space L.

If $x \in L$, then these differential quotients do not necessarily (o)-converge towards $x(s)$ in L. The following simple example shows this:

$$x(t) = \frac{n!}{n \lg^2 n} \text{ for } \frac{1}{(n+1)!} < t \leqslant \frac{1}{n!}. \qquad (n = 1, 2, \ldots)$$

The following theorem is therefore of some interest.

If $x \in L$, then the functions $U_I(x, s)$ (o)-converge towards $x(s)$ in the space $L_T(^2)$, where $T(u) = \dfrac{u}{(1 + \lg_2^+ u)^{1+\varepsilon}}$.

In view of Theorem 6 it is sufficient to prove that $x^* \in L_T$. Denote

$$E_N = E(x^*(s) > N).$$

We can enclose every point of E_N with such interval I that

$$\int_I |x(t)|\, dt > N \cdot |I|.$$

In the set of these intervals we can choose a subset of intervals no two of which have common points and such that the sum of the lenghts of these intervals is $\geqslant \frac{1}{3} mE_N$.

Let S be their sum; we have then evidently

$$\frac{1}{3} mE_N \leqslant mS \leqslant \frac{1}{N} \int_S |x(t)|\, dt \leqslant \frac{1}{N} \int_a^b |x(t)|\, dt.$$

Hence,

$$\int_a^b T[x^*(t)]\, dt \leqslant (b-a) + \sum_{k=2}^{\infty} \int_{E_{2k-1} - E_{2k}} T[x^*(t)]\, dt \leqslant (b-a) +$$

$$+ \sum_{k=2}^{\infty} \frac{2^k}{(1 + \lg_2 2^{k-1})^{1+\varepsilon}} mE_{2k-1} \leqslant (b-a) + \Big(\sum_{k=2}^{\infty} \frac{6}{k^{1+\varepsilon}}\Big) \int_a^b |x(t)|\, dt.$$

§ 3. Let l^2 be the space of such sequences $x = (a_1, a_2, \ldots)$ that $\sum_{i=1}^{\infty} a_i^2 < +\infty$ and let $\{\varphi_i(t)\}$ be a system of orthogonal and normal functions in the segment (a, b). Consider the sequence of operations

$$y = U_n(x) = \sum_{k=1}^{n} \frac{a_k}{1 + \lg k} \varphi_k \qquad (\lg k = \lg_2 k)$$

transforming l^2 into L^2.

We shall prove that the sequence $U_n(x)$ (o)-converges in L^2 for any $x \in l^2$.

As the convergence of $U_n(x)$ on the elements x of the form $(a_1, a_2, \ldots, a_n, 0, 0, 0, \ldots)$ (constituting an everywhere dense set in l^2) is evident, it remains to prove that the sequence $U_n(x)$ is (o)-bounded for every $x \in l^2$.

Denote $s_{h,j}(x) = U_{h2^{j+2^{j-1}}}(x) - U_{h2^j}(x)$ and

$$T(x) = |U_1(x)| + \sum_{j=1}^{\infty} |s_{\frac{1}{2},j}(x)| + \Big\{ \sum_{j=1}^{\infty} \sum_{h=1}^{\infty} (j + \lg h) |s_{h,j}(x)|^2 \Big\}^{\frac{1}{2}}.$$

Then: 1) $T(x) \in L^2$. In fact

$$\|T(x)\|_{L^2} \leqslant \|U_1(x)\| + \sum_{j=1}^{\infty} \|s_{\frac{1}{2},j}(x)\| + \Big\{ \sum_{j=1}^{\infty} \sum_{h=1}^{\infty} (j + \lg h) \|s_{h,j}(x)\|^2 \Big\}^{\frac{1}{2}} \leqslant$$

$$\leqslant |a_1| + \sum_{j=1}^{\infty}\Big[\sum_{k=2^{j-1}+1}^{k=2^j} \frac{a_k^2}{(1+\lg k)^2}\Big]^{\frac{1}{2}} + \Big\{\sum_{j=1}^{\infty}\sum_{h=1}^{\infty}\sum_{k=h2^j+1}^{k=h2^j+2^{j-1}} \frac{a_k^2}{1+\lg k}\Big\}^{\frac{1}{2}} \leqslant$$

$$\leqslant |a_1| + \sum_{j=1}^{\infty}\frac{1}{j}\Big(\sum_{k=2^{j-1}+1}^{k=2^j} a_k^2\Big)^{\frac{1}{2}} + \Big\{\sum_{k=1}^{\infty} a_k^2\Big\}^{\frac{1}{2}} \leqslant |a_1| +$$

$$+ \Big(\sum_{j=1}^{\infty}\frac{1}{j^2}\Big)\Big(\sum_{k=1}^{\infty} a_k^2\Big)^{\frac{1}{2}} + \Big(\sum_{k=1}^{\infty} a_k^2\Big)^{\frac{1}{2}} \leqslant 4\,\|x\|_{l^2}.$$

2) $|U_n(x)| \leqslant T(x)$ for every $x \in X$ and for $n = 1, 2, \ldots$

Let

$$n = \theta_1 + \theta_2 2 + \theta_3 2^2 + \ldots + \theta_r 2^{r-1} + 2^r, \qquad (\theta_i = 0, 1).$$

Then we have (for h_j suitably chosen)

$$|U_n(x)| = |U_{2^r}(x) + \sum_{j=1}^{r}\theta_j s_{h_j, j}(x)|.$$

Applying now the inequality of Cauchy and taking into consideration that $2^r \leqslant h_j 2^j$, we obtain

$$|U_n(x)| \leqslant |U_{2^r}(x)| + \Big\{r\sum_{j=1}^{r}|s_{h_j, j}(x)|^2\Big\}^{\frac{1}{2}} \leqslant |U_1(x)| +$$

$$+ \sum_{j=1}^{r-1}|s_{\frac{1}{2}, j}(x)| + \Big\{\sum_{j=1}^{r}(j+\lg h_j)\,|s_{h_j, j}(x)|^2\Big\}^{\frac{1}{2}} \leqslant T(x).$$

We have proved thus the «o-boundedness» of the sequence $\{U_n(x)\}$ and thereby we have proved also the proposition enunciated above. It is easy to see that the proposition just proved is the well-known theorem of Menshoff and Rademacher [5] on the orthogonal series, only a little generalized. The proof was also based on Rademacher's idea.

Note that the limit operation $U(x) = \sum_{k=1}^{\infty}\frac{a_k}{(1+\lg k)}\varphi_k$ is of the class H_1', but is not in general of the class H_0^0.

Mathematical Institute,
University of Leningrad.

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MATHEMATIK

ÜBER EINEN SATZ VON LIAPOUNOFF

Von K. PERSIDSKIJ

(Vorgelegt von A. N. Krylov, Mitglied der Akademie, d. 20. II. 1937)

Es sei $\varphi = \varphi(x_1, x_2, \ldots, x_n, t)$ eine Funktion der reellen Variablen $x_1, \ldots, x_n, t$, die reell und stetig in jedem Punkt $x = x(x_1, x_2, \ldots, x_n)$ des x_2, Bereiches

$$x_1^2 + x_2^2 + \ldots + x_n^2 < r^2 \qquad (A)$$

und für jeden Wert eines gewissen Intervalls

$$0 \leqslant t < t(x) \qquad (B)$$

ist, wobei $t(x)$ im allgemeinen von der Wahl des Punktes x abhängt. Wir nehmen an, die Funktion φ verschwinde in Punkt $O(x_1 = x_2 = \ldots = x_n = 0)$ für jeden Wert des Intervalls $0 \leqslant t < t(0) = \infty$. Dann wollen wir solche Funktion φ die Funktion der Klasse L nennen.

Nimmt eine Funktion φ der Klasse L in jedem Punkt x des Bereiches (A) und für jedes t am (B) Werte von demselben Vorzeichen an, so nennen wir diese Funktion permanent.

Ferner nennen wir eine permanente Funktion definit, falls sie auf der Fläche

$$x_1^2 + x_2^2 + \ldots + x_n^2 = \rho^2,$$

wobei $\rho > 0$ jede Zahl $< r$ bedeutet, der Ungleichung

$$|\varphi| \geqslant \lambda(\rho)$$

genügt, wo $\lambda(\rho)$ eine von Null verschiedene Zahl ist, die im allgemeinen von ρ abhängt. Hat dabei $t(x)$ in einem Punkt x des Bereiches (A) und für das Intervall (B) einen endlichen Wert, so nehme ich an, dass der Wert von $|\varphi|$ der Ungleichung

$$|\varphi| \geqslant M$$

genügt, wobei M konstant für alle Punkte des Bereiches (A) ist, falls die Werte von t zu $t(x)$ genügend nahe gelegen sind.

Ist $t(x) = \infty$ für jeden Punkt x des Bereiches (A), so sind die Funktionen der Klasse L nichts anderes als Liapounoffsche Funktionen (1).

Wir wollen ein System von Gleichungen

$$\frac{dx_s}{dt} = \omega_s(x_1, x_2, \ldots x_n, t) \qquad (s = 1, 2, \ldots n) \qquad (1)$$

betrachten, deren rechte Seiten in jedem Punkt des Bereiches

$$x_1^2 + x_2^2 + \dots x_n^2 \leqq R^2$$

und für alle $t > 0$ reell und stetig sind und stetige partielle Ableitungen erster Ordnung nach $x_1, x_2, \dots, x_n$ besitzen; wir nehmen dabei an, dass die ω_s im Punkte O für jedes $t \geqq 0$ verschwinden.

Es seien

$$x_s = f_s(t, c_1, c_2, \dots c_n) \qquad (s = 1, 2, \dots n) \tag{2}$$

Lösungen des Systems (1), die gleich c_s bei $t = 0$ sind, wobei $c_1, c_2, \dots, c_n$ gewisse reelle, der Bedingungen

$$c_1^2 + c_2^2 + \dots c_n^2 < R^2$$

genügende Konstanten bedeuten. Diese Lösungen existieren jedenfalls für diejenigen Werte von $t > 0$, bei denen die Ungleichung

$$f_1^2 + f_2^2 + \dots f_n^2 \leqq R^2$$

gilt. Bei diesen Werten von t die Funktionen $f_1, f_2, \dots, f_n$ besitzen stetige partielle Ableitungen erster Ordnung nach $c_1, c_2, \dots, c_n, t$, und die Jakobiane

$$\frac{D(f_1, f_2, \dots f_n)}{D(c_1, c_2, \dots c_n)} = e^{\int_0^t \sum \frac{\partial \omega_s(f_1, f_2, f_n, t)}{\partial f_s} dt}$$

ist von Null verschieden. Die Funktionen f_s verschwinden offenbar für $c_1 = c_2 = \dots c_n = 0$ bei jedem Wert von $t \geqq 0$.

Lösen wir das System von Gleichungen (2) nach $c_1, c_2, \dots c_n$:

$$c_s = \varphi_s(x_1, x_2, \dots, x_n, t), \quad \varphi_s = x_s \text{ für } t = 0, \tag{3}$$

so erhalten wir n unabhängige Integrale $\varphi_1, \varphi_2, \dots, \varphi_n$ des Systems (1).

Die Funktionen $\varphi_1, \varphi_2, \dots, \varphi_n$ sind stetig und besitzen stetige partielle Ableitungen erster Ordnung nach $x_1, x_2, x_3, \dots x_n, t$ wenn x im Bereiche

$$x_1^2 + x_2^2 + \dots + x_n^2 < R^2 \tag{A'}$$

liegt und $t > 0$ und genügend klein ist. Dieselbe Eigenschaft besitzen sie jedenfalls für alle Werte von t eines gewissen Intervalls

$$0 \leqq t < t(x) \tag{B'}$$

bei denen die Ungleichung

$$\varphi_1^2 + \varphi_2^2 + \dots + \varphi_n^2 \leqq R^2$$

gilt, wobei $t(x)$ im allgemeinen von der Wahl des Punktes x des Bereiches (A') abhängt. Es ist ersichtlich, dass im Punkte O die Funktionen φ_1, $\varphi_2, \dots \varphi_n$ für alle $t \geqq 0$ verschwinden.

Die Funktionen $\varphi_1, \varphi_2, \dots, \varphi_n$ gehören offenbar zur Klasse L; die Funktion

$$\varphi(x_1, x_2, \dots x_n, t) = \varphi_1^2 + \varphi_2^2 + \dots \varphi_n^2$$

ist stetig und positiv definit und besitzt stetige partielle Ableitungen erster Ordnung nach $x_1, x_2, \dots, x_n, t$ für jede Punkte des Bereiches (A'),

jedenfalls bei allen Werten vor $t > 0$, für die diese Funktion im gegebenen Punkt kleiner als R^2 oder gleich R^2 bleibt.

Ist die Lösung $x_1 = x_2 = \ldots = x_n = 0$ des Systems (1) stabil, so ist die Funktion $v = \varphi_1^2 + \varphi_2^2 + \ldots + \varphi_n^2$ positiv definit. Denn ist sie stabil, so gilt für jedes vorgeschriebene $\rho > 0$ die Ungleichung

$$f_1^2 + f_2^2 + \ldots + f_n^2 < \rho^2$$

sobald $c_1^2 + c_2^2 + \ldots + c_n^2 < \theta(\rho^2)$ ist, $\theta(\rho^2)$ — eine gewisse positive nicht abnehmende Funktion von ρ, die für $\rho \neq 0$ nicht verschwindet.

Dann gilt für jeden Punkt x des Bereiches (A′) und bei jedem t des Intervalls (B′)

$$v = \varphi_1^2 + \varphi_2^2 + \ldots + \varphi_n^2 \geqslant \lambda(\rho) = \theta(\rho^2),$$

wobei x auf der Fläche

$$x_1^2 + x_2^2 + \ldots + x_n^2 = \rho^2 \qquad (0 < \rho < R)$$

liegt. Denn nehmen wir an, dass diese Ungleichung in einem Punkt x des Bereiches (A′) und für einen Wert t' des Intervalls (B′), bei dem $v \leqslant R^2$ ist, nicht gilt, so kann man eine Lösung des Systems (1) finden derart, dass bei $t = t'$ und $c_1^2 + c_2^2 + \ldots + c_n^2 < \theta(\rho^2)$ die Gleichung

$$f_1^2 + f_2^2 + \ldots + f_n^2 = \rho^2$$

gilt, was unmöglich ist.

Damit die Lösung $x_1 = x_2 = \ldots = x_n = 0$ des Systems (1) stabil sei, ist die Existenz einer definiten Funktion v notwendig und hinreichend, deren totale Ableitung v' auf Grund der Gleichungen (1) entweder identisch verschwindet oder permanent und zu v von entgegengesetztem Vorzeichen ist, sobald $x_1, x_2, \ldots x_n, t$ solche Werte erhalten, bei denen die Funktion v definit bleibt. Dieser Satz ist eine Umkehrung des bekannten Satzes von Liapounoff (1) für Funktionen der Klasse L.

Es war schon bewiesen, dass im Stabilitätsfalle die Funktion

$$v = \varphi_1^2 + \varphi_2^2 + \ldots + \varphi_n^2$$

definit ist, während ihre totale Ableitung auf Grund der Gleichungen (1) identisch verschwindet. Nehmen wir z. B.

$$v = (\varphi_1^2 + \varphi_2^2 + \ldots + \varphi_n^2)(1 + e^{-t}),$$

so ist diese Funktion ebenfalls definit, während ihre totale Ableitung v' auf Grund der Gleichungen (1):

$$v' = -(\varphi_1^2 + \varphi_2^2 + \ldots + \varphi_n^2)\, e^{-t}$$

permanent den zum v entgegengesetzten Vorzeichen behält, sobald $x_1, x_2, \ldots, x_n, t$ die Werte durchlaufen, bei denen v definit bleibt. Daraus folgt die Notwendigkeit der Bedingungen des erwähnten Satzes.

Der Beweis der Hinlänglichkeit der im Satze formulierten Bedingungen ist elementar und weicht vom Beweise des erwähnten Liapounoffschen Satzes nur sehr wenig ab.

Institut für Mathematik und Mechanik
an der Universität Kazan.

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d. 20. II. 1937.

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PHYSICS

INFLUENCE OF CCl_4 VAPOUR ON PUNCTURE VOLTAGES OF AIR

By G. M. KOVALENKO

(Communicated by S. I Wawilow, Member of the Academy, 15. II. 1937)

In studying the length of spark of different gases Natterer (1) found that, at a given voltage and at equal pressure, a spark generated in CCl_4 vapour is longer than one generated in any other gas. While using a Van de Graaff electrostatic generator, Joliot(2) observed that the evaporation of liquid CCl_4 in the room containing the generator caused a considerable rise in the electric strength of the air. Neither Natterer nor Joliot, however, give any quantitative data as to the puncture voltages of either the CCl_4 vapour itself, or its mixtures with air.

The purpose of this work was to obtain quantitative data as to the puncture voltages of CCl_4 vapour and of its mixtures with air, with various forms of voltage and with varying configurations of the field.

All the puncture voltage measurements were made in a spherical glass vessel, of 4 litre capacity. In the case of an uniform field, steel spheres, 15 mm in radius, were used as electrodes; in the case of a non-uniform field, one of the spheres and a needle were used as electrodes. One of the electrodes could be easily displaced, and the distance read, without altering the pressure within the vessel. The vessel used in the experiments was evacuated with an oil pump. The pressures within the vessel were measured with a mercury gauge. Voltage was supplied to the electrodes from a plant consisting of a 2 kVA transformer and of a kenotron, either alternating or continuous voltage being obtainable by suitable switching. The puncture voltages at the impulses were measured with a special appliance, the duration of the impulse being about $2 \cdot 10^{-5}$ sec. To avoid lagging in measuring puncture voltages at the impulses, the spark gap was irradiated with a 60 mg radium preparation.

We give below the puncture voltage values for the first punctures in a given portion of CCl_4 vapour, or in the mixtures with air. These values, however, are practically identical with the mean values obtained from scores of punctures in the same portion of gas.

The following measurements were made:

1) Puncture voltages in CCl_4 vapour and in air were measured under the same conditions. Fig. 1 shows the results of measurements of puncture voltages in air and CCl_4 vapour, at a pressure of 60 mm and at a temperature of 16.5° C, with varying distances between the electrodes.

It may be seen from Fig. 1 that the puncture voltages of CCl_4 vapour are much greater than those of air, the ratio of puncture voltages decreasing

as the distance between the electrodes increases. During the measurements of puncture voltages in CCl_4 vapour, a black substance, apparently carbon, was deposited on the electrodes. Simultaneously, there appeared on the surface of the mercury, in the pressure-gauge tube communicating with the vessel, a whitish substance, in all probability $HgCl_2$, which in course of time diffused into the mercury.

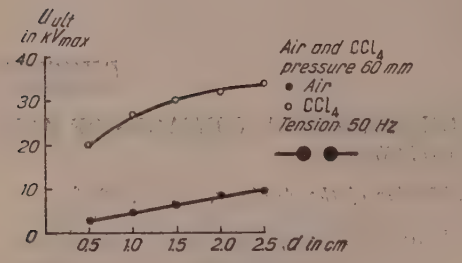

Fig 1.

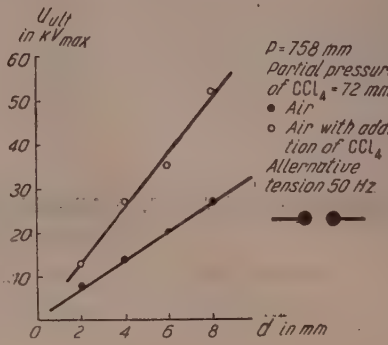

Fig. 2.

2) With a view to comparing the puncture voltages of air with those of mixtures of air with CCl_4 vapour at maximum saturation, measurements were made, the results of which are shown in Fig. 2.

The above data show that the addition of CCl_4 vapour to air is an effective means of raising the puncture voltages of the latter. Within the limits of

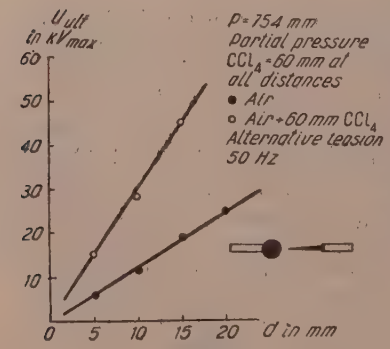

Fig. 3.

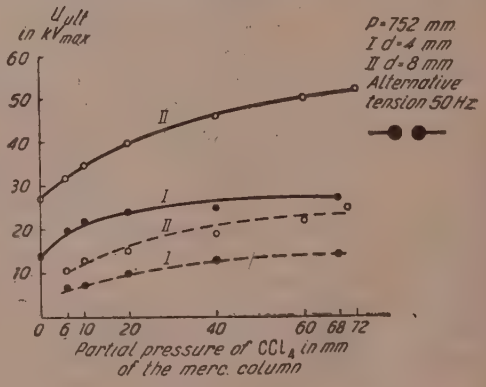

Fig. 4.

our measurements, the puncture voltages in an uniform field were increased 1.8 times if the air had been saturated with CCl_4 vapour. When an electric discharge takes place, the electrodes are exposed to the action of chlorine, that is evolved if the discharge occurs in CCl_4 vapour, and their surface deteriorates considerably. Before every new series of measurements, the electrodes were carefully cleaned and polished.

3) The results of the measurements made with non-symmetrical electrodes (needle-sphere) are shown in Fig. 3.

As may be seen from the above data, the relative rise of puncture voltages of air due to admixtures of CCl_4 is greater in a non-uniform field than in an uniform one. Within the limits of our measurements, the relative increase was about 2.5 times.

4) The results of the measurements of puncture voltages in mixtures of air with CCl_4 vapour in connection with the concentration of the latter in the air are given in Fig. 4. The same figure shows the puncture voltages of CCl_4 vapour for the case when the pressures of the vapour correspond to its partial pressures in the mixture.

These data warrant the conclusion that, in a mixture of air and CCl_4 vapour, the value of the puncture voltage is a sum of the puncture voltages of CCl_4 vapour and air, at pressures corresponding to the partial pressures of these components in the mixture.

The latter is in good agreement with Table 1, which shows the puncture voltages in a mixture of air and CCl_4 vapour and the sum of the puncture voltages obtained separately in air and in CCl_4 vapour at pressures corresponding to their partial pressures in the mixture.

Distance between electrodes	Puncture voltages in air		Puncture voltages in CCl_4 vapour		Sum of columns 2 and 3		Puncture voltages in mixtures of air and CCl_4 vapour	
1	2		3		4		5	
4 mm	684	13.000	68	13.50	752	26.50	752	27.00
	712	13.70	40	13.00	752	26.70	752	25.00
	732	14.50	20	10.00	752	24.50	752	24.00
8 mm	680	26.00	72	25.50	752	51.50	752	52.00
	712	26.00	40	19.00	752	45.00	752	46.00
	732	27.50	20	14.00	752	41.50	752	40.00

5) Fig. 5 shows the measurements of the dependence of puncture voltages on the concentration of CCl_4 vapour in the air at continuous voltage and different polarities in a non-uniform field, the distance between the electrodes being 8 mm.

6) The results of measurements made at the impulses lasting *ca.* $2 \cdot 10^{-5}$ sec., are given in Fig. 6.

7) Fig. 7 shows the results of measurements of puncture voltages of air in connection with CCl_4 vapour concentration in it. Spheres were used as electrodes, the duration of the impulse being the same as in the case of measurements shown in Fig. 6. The measurements were made at distances $d=5$ mm and $d=10$ mm.

The data appearing in Fig. 5, 6 and 7 show that the increase of puncture voltages is also observed with an impulse voltage and is manifested to an equal extent, independently of polarity, in markedly non-uniform fields. This shows that the increase is not connected with any peculiarities in the generation of space charges.

8) To elucidate the question of the influence exerted by an admixture of CCl_4 vapour on the puncture voltages of air at different pressures, measurements were made of puncture voltages of air mixtures with CCl_4 vapour, at constant vapour concentration, but at varying pressures. All the measurements were made at pressures below atmospheric pressure. The measurement results are given im Fig. 8, which shows the ratio of puncture voltages of the

mixture to those of air as a function of pressure, under identical conditions. As shown by these data this ratio of puncture voltages consistently decreases as the gas pressure increases.

The length of the free path of molecules in CCl_4 vapour is known to be only one-third of that in air. This fact alone, however, cannot directly account

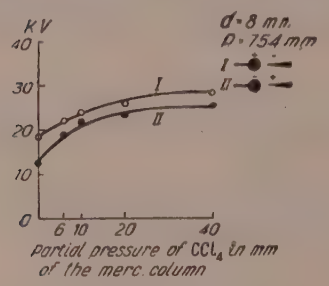

Fig. 5.

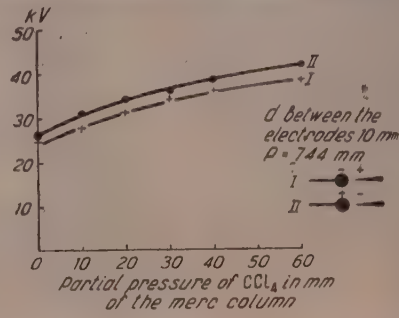

Fig. 6.

for the high electrical strength of CCl_4, as compared with air, and for its influence on the strength of its mixtures with air at low concentrations.

It is evident that, in colliding with the molecules of CCl_4, the charged particles moving in the electric field lose their charge, and this prevents them from accumulating an amount of energy sufficient for ionization.

A more definite solution of this question demands data on the value of the ionization potential and on the spectrum of excitation of the molecule of CCl_4, which are not at present available.

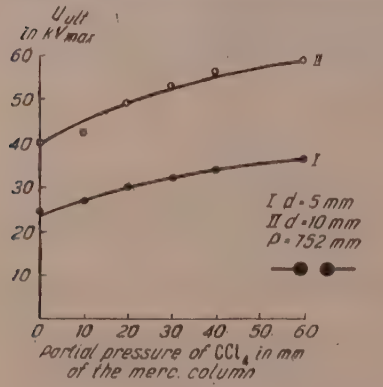

Fig. 7.

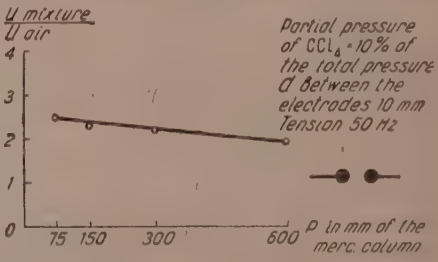

Fig. 8.

An admixture of an electrically stronger gas added to the air with a view to increasing its electrical strength, does not itself remain stable under all conditions, since electrical discharges cause its chemical decomposition, with the evolution of products lowering the electrical strength of the mixture. In the case under consideration, the CCl_4 is also decomposed by an electrical discharge, but the products evolved (carbon black and chlorine) do not lower the electrical strength of the mixture.

Lebedev Physical Institute.
Academy of Sciences of the USSR,
Moscow.

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PHYSICAL CHEMISTRY

KINETICS OF WETTING AND LINEAR CORROSION OF METALS IN POLYPHASE SYSTEMS: METAL—LIQUID—LIQUID AND METAL—LIQUID—GAS. II

By D. I. MIRLIS

(Communicated by V. A. Kistiakovski, Member of the Academy, 16. II. 1937)

In the first communication(1) we have shown that the changes in the contact angle characterizing the selective wetting of metals, which occur in the process of the spreading of a drop of water or of an aqueuos solution of an electrolyte over a metal surface immersed in benzene, are connected with the hydrophilization of the metal surface produced by the products of corrosion accumulated on the surface near the wetting perimeter. In this way it has been demonstrated that the kinetics of the contact angle under the conditions of the selective wetting of metals may serve as a sensitive and, moreover, a quantitative criterion of the change in the nature of their surface in the process of corrosion.

The subject of the present investigation as well as of the forthcoming ones is the study of the peculiarities of the corrosion process in three-phase systems: metal—liquid—liquid and metal—liquid—gas.

The interfacial corrosion of metals is associated with a number of interesting peculiarities whose elucidation might throw a good deal of light upon the general mechanism of the development of corrosion.

The problem of the corrosion of iron in the case of polyphase contact, which has been originally tackled by V. A. Kistiakovski(2), especially in his classification of the processes of iron corrosion, is now being successfully studied by his school. Apart from the highly interesting studies of V. A. Kistiakovski(3), the following investigations relating to the same subject are interest: a study of the behaviour of copper in the system water—ligroin in presence of sulphides by A. Wood, I. Sheely and A. Trusty(4), the investigations of I. D. Bengough and L. Whitby(5), and those of Evans(6), devoted to the corrosion of iron under an electrolyte drop at the contact with air (iron—3 per cent solution of NaCl—air). Most of the above authors, however, in interpreting their respective experimental results, skipped the problem of polyphase contact, for which reason they failed to ascend to any theoretical generalizations. Evans, for example, interprets his experimental results in terms of the theory of differential aeration. This theory, however, even if we adopt Evans' point of view, is only correct within narrow limits of concentrations of hydrogen ions, in which aeration, on a level with other factors, does produce some influence upon the process of corrosion. However,

when the pH range is extended on either the acid (pH=3 to 2) or alkaline side (pH=9 to 10), the importance of the aeration factor, and simultaneously of the theory of differential aeration, becomes greatly reduced. A critical analysis of the whole literature related to the subject affords no sufficient data to form a decisive conclusion regarding the mechanism of corrosion.

In studying the corrosion of metals under the conditions of their contact with the interface between an aqueous electrolyte solution and a non-polar organic liquid, the author used the method which had been described in his first communication (1). As has already been shown by the author, this method affords the possibility of quantitatively recording the kinetics of the corrosion process by observing the changes in the contact angle characterizing the selective wetting. In order to measure the contact angle in a metal—liquid—gas system, this method was somewhat modified*: a plane-parallel vessel was filled to one third of its volume with eihter water or an aqueous solution of the required electrolyte. The metal to be tested was fixed on a platinum holder above the liquid in the plane-parallel vessel, and a drop of the «aggressor» was placed on the metal surface, whereupon the vessel was carefully closed with a ground glass plate. In this way equilibrium systems, metal—liquid—gas (air), were obtained. The drop was projected to a screen in the usual way, the image was photographed, and the contact angles of wetting were measured on the photographs. Using this method, the kinetics of the corrosion process were studied for the following systems: Cu—water—benzene, Cu—3 per cent aqueous solution of NaCl—benzene, Cu—3 per cent aqueous solution of NaCl—air, Fe—water—air, Fe—3 per cent aqueous solution of NaCl—air, Fe—normal aqueous solution of HCl—benzene and Fe—normal aqueous solution of HCl—air. Armko iron and chemical pure copper were used. The data obtained for the kinetics of wetting are given in Table 1 in which Θ_{12} is the contact angle of wetting, and $B_{12}=\cos\Theta_{12}$. The experimental data given in this paper as well as the results published in the first communication afford the conclusion that the process of corrosion of metals with different «aggressors» (H_2O, NaCl, HCl etc.) is of the same character, although, as may be seen from the data of the Table, the individual experiments differ in the rate of development of the process. The results also depend upon the nature of the film on the metal surface, upon aeration and other factors. In presence of protective substances in the «aggressor», the parallelism between the variation of the contact angle in the course of time and the loss of weight undergone by the metal becomes particularly manifest.

If after a definite interval of time (3 to 24 hours from the start of the experiment) the metal plate is cleaned of the products of corrosion, and the corroded area is next gently polished with fine emery paper, then in all cases a regularly shaped circle (or rather an ellipse) may be seen along the line of contact with the aqueous solution of the electrolyte and the non-polar hydrocarbon medium, the character of the spreading of the drop being connected with the anisotropic nature of the surface (Fig. 1). The same phenomenon (which is especially interesting) is to be observed in the system metal—liquid—air. The depth of the boundary affection of metals varies with the nature of the «aggressor». When the role of the «aggressor» is played by distilled water, the boundary corrosion barrier is faintly expressed, whilst under the action of NaCl solutions it is more manifest, and finally in the case of hydrochloric acid or other acids, the boundary corrosion is of a more

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* Presented at the meetings of the Scientific Board of Colloid-Electrochemical Institute on March 13 and June 3, 1936.

$B_{12} = \cos \Theta_{12}$

Time in min.	Cu — water — benzene		Cu—3 p. c. aq. sol. of NaCl — benzene		Cu—3 p. c. aq. sol. of NaCl— air		Fe — water — air		Fe—3 p. c. aq. sol. of NaCl — air		Fe — norm aq. sol. of HCl — benzene		Fe — norm. aq. sol. of HCl — air	
τ	Θ_{12}	B_{12}	Θ_{12}	B_{12}	Θ_{12}	B_{12}	Θ_{12}	B_{12}	Θ_{12}	B_{12}	Θ_{12}	B_{12}	Θ_{12}	B_{12}
0	128	−0.616	124	−0.559	93	−0.052	70	+0.342	66	+0.407	111	−0.358	33	+0.839
1	—	—	117	−0.454	93	−0.052	68	+0.374	53	+0.602	55	+0.573	24	+0.913
3	121	−0.515	104	−0.242	93	−0.052	64	+0.438	31	+0.857	54	+0.588	23	+0.920
5	117	−0.453	90	0.000	93	−0.052	60	+0.500	30	+0.866	54	+0.588	21	+0.935
9	106	−0.275	75	+0.259	90	0.000	58	+0.530	29	+0.875	51	+0.629	20	+0.940
17	106	−0.275	62	+0.469	90	0.000	57	+0.545	29	+0.875	51	+0.629	20	+0.940
34	106	−0.275	59	+0.515	86	+0.069	55	+0.573	29	+0.875	49	+0.642	20	+0.940
64	100	−0.174	54	+0.588	72	+0.309	54	+0.588	27	+0.891	46	+0.695	16	+0.961
124	100	−0.174	52	+0.616	54	+0.588	44	+0.710	25	+0.906	40	+0.766	13	+0.974
199	100	−0.174	52	+0.616	48	+0.669	38	+0.788	22	+0.927	38	+0.788	—	—
319	98	−0.139	52	+0.616	43	+0.731	—	—	—	—	—	—	—	—
409	—	—	—	—	—	—	—	—	—	—	—	—	—	—
24hours	86	+0.069	36	+0.809	21	+0.923	—	—	—	—	—	—	—	—

concentrated nature with greater depth of affection*. In our cases linear corrosion is more clearly expressed on iron than on copper. The above results enable us to state with certainty that, under the conditions of polyphase contact, the process of corrosion is of a linear nature.** The phenomenon of linear corrosion discovered by the author in the systems metal—liquid—liquid and metal—liquid—gas is to be observed wiht the majority of metals, and is of great importance for the study of flotation. A similar phenomenon of linear corrosion under somewhat different conditions was detected by the author in collaboration with L. G. Gindin and F. M. Shemiakin in the system metal—paraffin—electrolyte.

Fig. 1. Armko iron plate after corrosion in three-phase system; metal-water-benzene.

In the systems Fe—aqueous solution of HCl—benzene and Fe—aqueous solution of HCl—air, the liberation of hydrogen as a result of corrosion proceeds chiefly at the three-phase boundary line.

The hydrogen bubbles liberated along the periphery are conveyed to the centre of the drop where they pierce its surface and escape.

A similar phenomenon of liberation of hydrogen bubbles was observed, under somewhat different conditions, by one of the representatives of the school

* In presence of surface active substances in the «aggressor» (mineral acids), a series of concentric circles is to be observed, i. e. the process of corrosion is of a periodic nature.

** The same effect was observed by the author in the benzene phase of the system: Fe—aqueous solution of propionic acid—benzene, which will constitute the subject of one of the forthcoming communications.

of the Academician A. N. Frumkin, namely by B. Kabanow ([7]) while he studied the mechanism of electrolytic degreasing of metals.

When the role of the «aggressor» is played by distilled water, aqueous solutions of neutral salts incapable of passivating the metal (e. g., NaCl), or dilute solutions of mineral acids (HCl, H_2SO_4), the course of the process of corrosion is qualitatively somewhat different [(aeration and other factors manifesting themselves in these media (Fig. 2)], and though the final effect of linear corrosion still exists, it is somewhat less conspicuous.

It was thus experimentally established that the three-phase boundary (in metal—liquid—liquid and metal—liquid—gas) systems constitutes the region which, in the main, is responsible for the phenomenon of corrosion. However, the mechanism in virtue of which corrosion chiefly proceeds along the three-phase boundary line is not yet clear enough, and constitutes the object of our further research.

Fig. 2. Three-phase system: iron—3 p. c. aqueous solution of NaCl—benzene.

Conclusions: 1. It has been shown experimentally that the corrosion of metals under the conditions of polyphase contact (metal—liquid—liquid and metal—liquid—gas) is of a linear character.

2. It has been experimentally ascertained by studying the variation of the contact angle of wetting with time that the process of corrosion of metals (in particular iron) in polyphase systems metal—liquid—liquid and metal—liquid—gaz exhibits selective localization not in the centre as might be expected on the basis of the differential aeration theory, but mainly along the phase boundary line in perfect agreement with the classification advanced by V. A. Kistiakovski and with the phenomenon of linear corrosion studied by the present author.

3. The experimental data obtained throw doubt upon the exceptional importance of the differential aeration factor in the development of the process of corrosion in the systems: metal—liquid—liquid and metal—liquid—gas.

4. It has been ascertained that the changes undergone by the molecular nature of a metal surface in equilibrium systems metal—liquid—gas in the course of time may be quantitatively recorded by measuring the contact angle of wetting.

Colloid-Electrochemical Institute.
Academy of Sciences of the USSR.
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CHEMISTRY

THE ACTION OF THE HALOGEN COMPOUNDS OF ARSENIC AND PHOSPHORUS ON ETHINCARBOXYLIC ACIDS

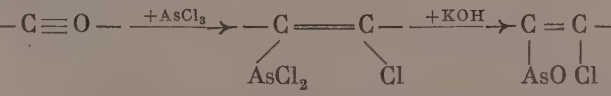
I. ON THE ADDITION REACTION OF ARSENIC CHLORIDE WITH TETROLIC ACID

By V. O. MOCHNAČ and V. S. BAGNIUK

(Communicated by A. E. Favorskij, Member of the Academy, 23. I. 1937)

In 1913, Emil Fischer and Georg Klemperer published a paper (1) on the method of preparing and the pharmacological action of a new arsenic compound—elarson, which achieved a wide medical application. To judge from the method of its preparation, it is a strontium salt of «chlorarsenobehenolic» acid, which is obtained by the action of arsenic chloride on behenolic acid. The structure of chlorarsenobehenolic acid cannot be exactly determined; however, in the opinion of the authors, «there can hardly be any doubt about the addition of chlorine and arsenic to carbon belonging to the unsaturated group»(1).

In the following year, E. Fischer (2) published more detailed information regarding a new class of aliphatic arsenic compounds. After unsuccessful attempts to effect the addition of arsenic chloride to ethylene derivatives, he was able, to a certain extent, to obtain the reaction in respect to behenolic acid according to the formula:



However, in this case, it was likewise impossible to isolate the product of the addition reaction; the reddish-brown oil-like liquid, to judge from the analyses, was a mixture, 86 per cent of which was chlorarsinosobehenolic (chlorarsenobehenolic) acid (in the residue, probably, there was behenolic acid which had not reacted to completeness). E. Fischer was inclined to attribute the failure of his attepmts to obtain chlorarsinosobehenolic acid in crystalline form to the probability that during the addition reaction of the AsO-group and chlorine with behenolic acid a complex mixture of two structural isomeres and two stereoisomeres resulted. An attempted addition reaction of arsenic chloride with stearolic acid gave still less satisfactory results.

Still, further conversions of chlorarsinosobehenolic acid (synthesis of chlorbehenolmethylesterarsinic acid), together with indirect analyses and a consideration of the method of preparation, enabled E. Fischer to accept the above-shown scheme as showing the addition of arsenic chloride at the triple bond.

In view of the fact that the higher ethinic acids thus afford a rather unsatisfactory initial material for investigating this reaction, E. Fischer thought it best to study the lower homologues of the fatty series in this connection. However, the difficulties of synthesizing them compelled him to resort to phenylpropiolic acid, which, indeed gave crystallizing products, but of a somewhat different type, concerning which he proposed to publish supplementary information. Unfortunately, neither E. Fischer himself nor other authors([3—7]) went into the problem in detail from a chemical point of view.* There is only a statement by G. Joachimoglu([8]) that the preparation of potassium arsenophenylpropiolate given him by E. Fischer for pharmocological investigation contained 17.36 per cent of arsenic, a statement which does not agree at all with the formula shown above. So that, although this formula may be taken as fairly probable for behenolic acid, still the question of the addition of arsenic chloride to ethincarboxylic acids with carboxyl at the triple bond remains unsolved.

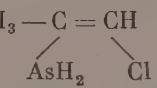
Inasmuch as the addition products of this sort have not only a theoretical interest but may have also a practical importance, a systematic study of the action of the halogen compounds of arsenic on ethincarboxylic acids was quite timely.

We began our investigation with tetrolic acid, as being one of the simplest in composition and as being easy to prepare owing to the recently found method of obtaining it by means of sodium amine. *A priori* it is not impossible that the action of arsenic chloride on behenolic and stearolic acids, on the one hand, and tetrolic or ethylpropiolic acid, on the other hand, may present certain differences, since in the first instance the acetylene bond is quite distant from the carboxyl, while in the case of acids of the type of propiolic acid, the bond is alongside. Consequently, the energetic interaction of functional factors located alongside is considerably weakened: in behenolic acid, for example, where the carboxyl group differs little from the carboxyl of the polyatomic saturated aliphatic acids, while the triple bond is similar to that of the hydrocarbons.

Our experiments with tetrolic acid (as also with ethylpropiolic) were conducted at first with a nice observance of the conditions laid down by E. Fischer. Only the operations connected with the separation of the reaction product from the behenolic acid were omitted—since our starting point, tetrolic acid, dissolves quite well in water and is easily separated off. The data obtained allow no doubt that the addition of arsenic chloride under these conditions is accompanied by a decarboxylation of the acid and the formation of products of hydrocarbon type. This may possibly be explained by the action of the caustic alkali or by the comparatively high temperature of the reaction; Moureu and Delanges have pointed out the extreme sensitiveness of the ethincarboxylic acids in this respect([9]). Our experiments showed that the influence of temperature predominates, since when it is lowered one succeeds in retaining the carboxyl, notwithstanding the usual treatment of the product with caustic alkali.

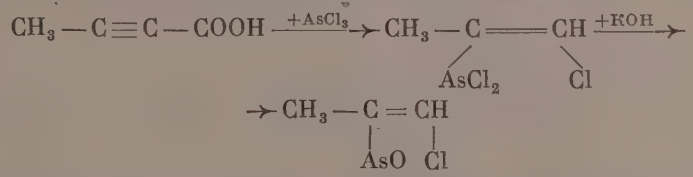
* The literature on patent preparations introduces some changes in Fischer's method. See the short review by G. W. Raiziss and J. L. Gavron in «Organic Arsenical Compounds». 1923, pp. 99—102 and 522—523.

The addition reaction of arsenic with tetrolic acid at a temperature of 140° (see experiment 1) gives, instead of the arsinoxy-acid contemplated by Fischer's formula, a beautifully crystallizing product which melts at 91. 5 to 92° and which, to judge from a number of analyses, corresponds to the formula C_3H_6AsCl. Its structure might be the following:



This product, which may be called chlorpropenylarsine, like the one which Fischer obtained from behenolic acid may, theoretically, exist in four isomeric forms; however, the sharply definite melting point indicates that here we have only one of them.

If the addition reaction be carried on under somewhat milder conditions (120 to 130°, see experiment 2), there is obtained an arsinoxy-derivative, but also decarboxylated (chlorarsinoxy-propene), according to the formula:



Finally, when the temperature is still further lowered, the addition reaction (see experiment 3) proceeds «normally», without destruction of the carboxyl. In the last case the product is a yellowish oil.

Analyses of the products obtained at temperatures ranging between those mentioned above give average figures indicating the formation of mixtures of arsenic derivatives.

Experiments conducted by A. Zatsarin with ethylpropiolic acid are in correspondence with the data we have given regarding tetrolic acid. With temperatures of 150 to 155° crystalline arsinoxy-derivative of the hydrocarbon type results (see experiment 4); at lower temperatures (130 to 140°, see experiment 5), a mixture of crystallizing products in which, judging from the analyses, arsinoxy-acid predominates.

It follows from these observations that:

1) When arsenic chloride acts on tetrolic acid under the conditions stated, there occurs a reaction of addition;

2) under temperatures of about 130 to 150° there occurs a decarboxylation of the acid with the formation of products of the hydrocarbon type;

3) one of the factors influencing the nature of the arsenic derivatives obtained is the temperature under which the reaction runs.

EXPERIMENTAL

I. The Action of $AsCl_3$ on Tetrolic Acid

Experiment 1. 2 grams of tetrolic acid (melting point 76.5°) and 6 grams of arsenic chloride (boiling point 130°) were placed in a small round-bottomed flask with backflow condenser equipped with a calcium chloride tube. The mixture was heated under the hood for six hours in an oil bath (temperature of the bath 135 to 140°). The reaction product—a thick,

dark brown liquid when cold, was dissolved in ether and carefully washed in distilled water. The ether solution separated from the water was evaporated; the residue diluted with alcohol (6 ml) was rapidly treated with a normal solution of caustic potash cooled to 0° and immediately acidulated with dilute hydrochloric acid. The resulting opaque liquid of a light yellow colour was three times extracted with ether, the ether extract was dried with calcium chloride, and the ether distilled. The residue left in the distilling flask was a thick brownish liquid, which quickly crystallized in the form of thin needles distributed star-fashion. Yield, 1.5 grams. The crystals dissolved well in alcohol and water, poorly in petroleum ether and cold water. When squeezed dry on filter paper, the crystals were absolutely colourless and had a melting point of 91.5 to 92°.

Analyses

1. Determination of chlorine (Karius):
a) 0.1056 grams of substance: 0.0997 grams AgCl;
b) 0.1300 » » » : 0.1232 grams AgCl;
Percentage found: a) Cl 23.33;
» » b) Cl 23.05;

C_3H_6AsCl. Calculated percentage: Cl 23.27.

2. Determination of carbon (Messinger):
0.1006 grams of substance: 0.0882 grams CO_2:
Percentage found: C 23.83.

C_3H_6AsCl. Calculated percentage: C 23.62.

3. Determination of hydrogen (by burning with copper oxide in the presence of lead bichromate):
a) 0.1702 grams of substance: 0.0692 grams H_2O
b) 0.1486 grams of substance: 0.0554 grams H_2O
Percentage found a) H 4.55
» » b) H 4.17

C_3H_6AsCl. Calculated percentage: H 3.94.

Experiment 2. 4 grams of tetrolic acid and 12 grams of arsenic chloride were heated under the hood in an oil bath at a temperature of 120 to 130° for six hours. The reaction product, a brownish liquid, was dissolved in ether and washed with distilled water (500 cm^3). The ether was distilled off, the residue was diluted with alcohol, treated with normal caustic potash (cooled to +3°) and then acidulated with dilute hydrochloric acid. The rest of the treatment was the same as in experiment 1. Yield, 3 grams. Almost all of the product crystallized.

Analyses

Determination of chlorine (Karius):
a) 0.0980 grams of substance: 0.0852 AgCl;
b) 0.1024 grams of substance: 0.0876 AgCl;
Percentage found: a) Cl 21.54;
» » b) Cl 21.19;

C_3H_4AsOCl. Calculated percentage: Cl 21.32.

Experiment 3. 2 grams of tetrolic acid and 6 grams of arsenic chloride were heated under the hood in an oil bath at a temperature of 110 to 115°. Treatment of the product was the same as in experiment 1. Yield, 1.7 grams (light yellow liquid).

Analyses

Determination of Chlorine (Karius):
a) 0.0520 grams of substance: 0.0346 grams AgCl;
b) 0.0964 grams of substance: 0.0670 grams AgCl;
Percentage found: a) Cl 16.49;
» » b) Cl 17.21;

$C_4H_4O_3AsCl$. Calculated percentage: Cl 16.87.

II. On the Action of $AsCl_3$ on Ethylpropiolic acid

(A. I. Zatsarin)

Experiment 4. 4 grams of ethylpropiolic acid and 12 grams of arsenic chloride were placed in a small round-bottomed flask with backflow condenser and equipped with a calcium chloride tube. The flask was heated under the hood in an oil bath (150 to 155°) for 8 hours. The reaction product, a dark brown liquid, was on cooling, diluted with ether (about 150 ml) and carefully washed with water.

The ether layer separated from the water was evaporated down to a small volume. The residue was diluted with 96 per cent alcohol, treated for 8 seconds with a normal solution of caustic potash cooled to 0°, and immediately neutralized with dilute hydrochloric acid. The resulting yellow solution was extracted with ether. The extract was dried with calcium chloride, and the ether distlled off. The residue was a thick brownish liquid which afterward partially crystallized. Yield, 3.5 grams.

Analyses

Determination of chlorine (Karius):
a) 0.1620 grams of substance: 0.1272 grams AgCl;
b) 0.1780 grams of substance: 0.1424 grams AgCl;
Percentage found: a) Cl 19.61;
» » b) Cl 19.82;

C_4H_6OAsCl. Calculated percentage: Cl 19.66.

Experiment 5. A mixture of 4 grams of ethylpropiolic acid and 12 grams of arsenic chloride was heated under the hood in an oil bath at a temperature of 130 to 140° for eight hours. The reaction product was treated as in experiment 4. Yield, 3.2 grams (yellow-brown liquid, which partially crystallized).

Analyses

Determination of chlorine (Karius):
a) 0.1744 grams of substance: 0.1214 grams AgCl:
b) 0.1837 grams of substance: 0.1273 grams AgCl:
Percentage found: a) Cl 17.40;
» » b) Cl 17.16;

C_4H_6AsCl. Calculated percentage: Cl 19.66.
$C_5H_6O_3AsCl$. Calculated percentage: Cl 15.81.

Laboratory of Organic Chemistry
of the Far Eastern-Branch of the Academy
of Sciences of the USSR and the Far-Eastern
State University.

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CHEMISTRY

CONCERNING THE GEOMETRICAL ISOMERISM OF HALOGEN-SUBSTITUTED ETHENE ACIDS

II. ADDITION OF HYDROGEN BROMIDE TO TETROLIC ACID

By V. O. MOCHNAČ and A. I. STOLIAROV

(Communicated by A. E. Favorskij, Member of the Academy, 23. I. 1937)

In the first investigation on this subject, Favorskij, with one of us (1), wrote on the synthesis of two geometrical isomeres (β-brome-α, β-pentene acids) by a single addition of hydrogen bromide to ethylpropyl acid. In order to prove the β-position of the halogen in the acids synthesized by us, it was necessary to obtain the α-isomeres as well. We were able to synthesize only one α-isomere; thus, one of the four theoretically possible (substituted at the double bond) monobrome pentene acids remained unknown. In the same work we cited the literary data on this question, which agree in reporting the β-position of the halogen in additions of this kind. Still neither these data nor even our experimental material are sufficient to entirely exclude the identity of our lower-melting isomere with the unknown α-isomere. This objection would evidently have no validity if the second α-isomere, different from the one we synthesized, were made known.

Consequently, in continuing our investigations, we decided to take tetrolic acid as the starting point; of the monobrome-substituted crotonic acids, both α-brome acids and one β-brome acid are already known.

α-bromisocrotonic acid [melting point 92° according to Michael and Norton(2); 90° according to Kolbe (3)] is obtained (along with other products, among them a higher-melting form) from both isomeres of α-, β-dibrombutyric acid (melting points 87 and 59°) by the process of splitting off hydrogen bromide. Under the action of caustic alkalis [Kolbe(4), Michael and Schulthess(5)] or of alcohol caustic potash (Michael and Norton(2)] on α-, β-dibrombutyric acid (melting point 87°) this lower-melting form is almost exclusively obtained.

α-bromcrotonic acid [melting point 106.5° according to Michael and Norton(2); 107—108° according to Pfeiffer(7)] is obtained from α_1-, α-dibrombutyric acid by the action of weak bases or alcohol solutions of caustic potash when heated [Michael and Norton(8) and others]. Through the action of aqueous alkalis on dibrombutyric acid (59°) there is obtained a mixture of almost equal parts of both α-acids. The lower-melting isomere changes into the higher-melting one when heated to 130—140° in sealed tubes [Michael and Pendleton (9); Michael and Schulthess (10) and likewise under the

action of pyridine—preferably with the addition of pyridine hydrochloride, Pfeiffer [11]].

α-bromcrotonic acid is obtained, as a rule, by the action of a hydrogen bromide solution saturated at 0° on tetrolic acid [Michael and Brown[12]]. A few hours after the crotonic acid is dissolved, long needles (melting point 75—83°) begin to precipitate from the solution. After repeated rercrystallization out of water, the melting point does not rise above 85°. Finally, after recrystallizing four times from petroleum ether, the product melts at 94.5—95°. Clutterbuck [13]), using this method, obtained, after repeated recrystallization, crystals melting at 93.5°. Melikoff[14]) synthesized bromcrotonic acid having a melting point of 94° by distilling β-brom-α-oxybutyric acid with sulphuric acid.

The work of Autenrieth to some extent disagrees with the data here presented on β-bromcrotonic acid. This writer hydrolyzed *n*-bromanilide of α-, β-dibrombutyric acid with hydrochloric acid at 130° and, amongst other products, obtained a monobrome acid melting at 97°[15]), which he took for the β-acid of Michael. It is more than probable, however, that what Autenrieth obtained was a mixture of α-isomeres (92, 107—108°) having a melting point of about 97°: all the data to be found in the literature assert that when HBr is split off from α-β-dibrombutyric acid, α-derivatives are always obtained.

In concluding this summary, it may be said that the probabilities are that two (92, 107—108°) of the three known bromcrotonic acids are α-stereoisomeres and one (94.5—95°) is a β-isomere. Synthesis of the fourth bromcrotonic acid is needed for complete confirmation of these correlations by chemical methods. An attempt in this direction by Michael gave a negative result. When phosphorus pentabromide acted on acetoacetic ether, he obtained crystals having a melting point of 85°[16]). The determination of bromine gave 29.13 per cent (theoretical: 48.48 per cent). In another of his investigations, the author found a bromine content of 18 per cent [17]).

The fact that a second β-isomere could not be separated in the addition reaction of bromine with tetrol, may be explained by too long a treatment of the addition products. It is quite probable that the «impure» products mentioned by some authors[18]), having a lower melting point than was required, contained a considerable quantity of a lower-melting stereoisomere. The less stable form which is usually obtained in considerably smaller quantity, is partly simply lost in the filtrate when repeatedly recrystallized and partly isomerized into a more stable form.

In order to shorten as much as possible the addition reaction of hydrogen bromide with tetrolic acid, we tried out heating to 40° the mixture of the acid with a hydrogen bromide solution saturated at 0°. As is to be seen from Experiment 1, we thus obtained a mixture of α, β-dibrombutyric acids, with probably a preponderance of the lower-melting (59°) form [melting point of the raw product is about 63—65°; after recrystallization from petroleum ether: 1) 70—71°, 2) 73—74°. A number of tests for bromine content gave figures answering exactly to the formula for dibrombutyric acid]. Heating to 25°, also with a solution of hydrogen bromide saturated at 0° (see Experiment II), gave the same result. Michael [19]), it would seem, got a similar mixture by heating to 100° α-bromcrotonic acid (106°) with a solution of hydrogen bromide saturated at 0° in sealed tubes. The raw product melted at 55—62°, after the first crystallization it melted at 70°. Further crystallization enabled Michael to obtain both dibrombutyric acids (58—59 and 87°). Our mixture of dibrombutyric acids was not subjected to separation, since that did not enter into the plan of our work.

It is thus evident that the saturation of water with hydrogen bromide at 0°, followed by a weak heating of the reacting mixture, results in too great an excess of the halogen-hydrogen capable of reacting over the «constantly boiling hydrate»([20]), or, more accurately speaking, over hydroxonium bromide: $Br—O—H_3$. Consequently, we used solutions of hydrogen bromide saturated at a higher temperature (20—25°). We hoped, through investigations of temperatures of saturation and temperatures of heating the reacting mixture, to be able to make a choice of conditions under which the reaction would run its course, first of all, quickly and, secondly, with the addition of only one molecule of hydrogen bromide to the triple bond. As Experiment III shows, the use of a solution of halogen-hydrogen saturated at 25° with subsequent keeping of the reaction mixture at 18—20° give, after a few hours, a good quantity of beautifully crystallizing monobromcrotonic acids. After recrystallization, two sharply differing fractions were found in the product obtained: a smaller one, having a melting point of 79—82° and a greater, having a melting point of 90—91°. It was repeatedly observed that, when preparations were simply kept in an empty exsiccator, with no treatment of them whatever,—the melting points of both fractions gradually rose. From the first fraction there was separated a product with a melting point of 80—81°; from the second, a product with a melting point of 94.4°. Analyses of the products for bromine and of the salts obtained from them correspond exactly to the formula for monobromcrotonic acid. Hence it may be concluded that as a result of a single addition of hydrogen bromide to tetrolic acid, two isomeric bromcrotonic acids were obtained.

To judge from the method of obtaining and the properties, one of them (melting point 94.4°) was the already known β-bromcrotonic acid, the other (melting point 80—81°) being its isomere, as yet unknown. A comparison of the literary data on these acids cited above with the experimental result we obtained permits the conclusion that bromcrotonic acids with melting points of 92 and 107—108° are α-stereoisomeres, while those melting at 80—81 and 94.4° are β-stereoisomeres.

In conclusion, we would like to direct attention to the interesting coincidence of difference in melting points of the two α-isomeres and the two β-isomeres. A still closer coincidence occurs in the case of chlorocrotonic acid; α-isomeres: 99.2° and 66°; β-isomeres: 94 and 61°.

EXPERIMENTAL

A. Preparation of Dibrombutyric Acids $C_4H_6O_2Br_2$

Experiment I

15 grams of distilled water were saturated at 0° in a glass cylinder with hydrogen bromide to an added weight of 30 grams. 3.9 grams of tetrolic acid were added, the cylinder was closed with a ground glass stopper and placed in a Schüttelapparat for eight hours and after that in a thermostat for 24 hours at 40°. The crystals that separated from the solution were filtered off, washed with water and dried in a thermostat at 40°. They are easily soluble in ether and alcohol, difficultly soluble in water. Melting point 63—65°.

After recrystallization from petroleum ether, the melting point was 70—71°.

Determination of bromine (Karius):
a) 0.1882 grams of substance: 0.2870 grams AgBr.
b) 0.1360 grams of substance: 0.2069 grams AgBr.
Percentage found: a) Br 64.89;
» » b) Br 64.74.
$C_4H_6Br_2O_2$. Calculated percentage: Br 65.01.

The same preparation showed a smaller bromine content after standing for 30 days with access of air.

Determination of bromine (Karius):
0.1131 grams of substance: 0.1617 grams AgBr.
Percentage found: Br 60.84.
$C_4H_6Br_2O_2.H_2O$. Calculated percentage: Br 60.58.
$C_4H_6Br_2O_2$. Calculated percentage: Br 65.01

After standing three days in the exsiccator over sulphuric acid, the bromine content in the preparation became higher again.

Determination of bromine (Karius):
0.1424 grams of substance: 0.2176 grams AgBr.
Percentage found: Br 65.03.
$C_4H_6Br_2O_2$. Calculated percentage: Br 65.01.

Experiment II

12 grams of distilled water were saturated with hydrogen bromide in a glass cylinder at 0°. To this solution 3.3 grams of tetrolic acid were added, and the cylinder was closed and left at a temperature of 15—16°. After eight hours, fatty drops had appeared on the surface of the solution, which fell to the bottom on shaking. Then, the solution was heated in a water bath to 25° for ten days, at the end of which period the oil had crystallized. The crystals were filtered off, washed with water and dried. Melting point 62—64°. After recrystallization from petroleum ether, there were obtained well-formed colourless rhomboid prisms which melted at 73—74°.

Determination of bromine (Karius):
0.2509 grams of substance: 0.3826 grams AgBr.
Percentage found: Br 64.89.
$C_4H_6Br_2O_2$. Calculated percentage: Br 65.01.

B. Preparation of β-Monobromcrotonic acid $C_4H_5O_2Br$

Experiment III

45 grams of distilled water were saturated with hydrogen bromide in a cylinder having a ground glass stopper at 25°. 12 grams of tetrolic acid were added, and the solution left over night. A large quantity of crystals precipitated during the night and were filtered off, washed with water and recrystallized from water twice. The crystals fell into two fractions sharply differing as regards their melting points: one melted at about 79°, the other at 90—91°.

Determination of bromine (Karius):
a) 0.1570 grams of substance: 0.1775 grams AgBr.
b) 0.1521 grams of substance: 0.1719 grams AgBr.
Percentage found: a) Br 48.12;
» » b) Br 48.09.
$C_4H_5O_2Br$. Calculated percentage: Br 48.48.

The preparation was recrystallized from petroleum ether.

1) The crystals (needles) were filtered off, pressed dry and left in the exsiccator over paraffine.* The melting point was determined the following day as being 90.5—93°. After standing twenty days in the empty exsiccator, the crystals melted at 94.4° sharp.

Analyses of β-bromcrotonic acid and its salts (higher-melting form):
Determination of bromine (Karius):
a) 0.1210 grams of substance: 0.1387 grams AgBr.
b) 0.1647 grams of substance: 0.1898 grams AgBr.
Percentage found: a) Br 48.78;
» » b) Br 48.77.
$C_4H_5O_2Br$. Calculated percentage: Br 48.48.

The sodium salt was obtained by the action of sodium carbonate on the acid. It crystallized out of the aqueous solution in the form of druses consisting of very fine needles. It is easily soluble in water and soluble with difficulty in alcohol.

a) 0.4608 grams of substance (dried at 105°): 0.1828 grams Na_2SO_4.
b) 0.3737 grams of substance (dried at 105°): 0.1485 grams Na_2SO_4.
Percentage found: a) Na 12.84;
» » b) Na 12.87.
$C_4H_4O_2BrNa$. Calculated percentage: Na 12.30

The calcium salt was prepared by the action of calcium carbonate on the acid. It separates from the solution in the form of a finely crystallized precipitate.

0.1523 grams of substance (dried at 105°), 0.0551 grams $CaSO_4$.
Percentage found: Ca 10.64
$(C_4H_4O_2Br)_2Ca$. Calculated percentage: Ca 10.87.

2) On evaporating the mother liquor (see above), crystals precipitated which, after standing for 24 hours over paraffine in the exsiccator, melted at 79—82°. From this fraction, a product was separated which had a melting point of 80—81°, and which crystallized in the form of very fine needles, comparatively easily soluble in hot water, less easily in cold. It dissolves considerably better in petroleum ether than does the higher-melting isomere. After the crystals had been left 20 days in the empty exsiccator, their melting point rose to 87—89°.

Analyses of β-bromcrotonic acid and its calcium salt (lower-melting form):
Determination of bromine (Karius):
0.0681 grams of substance: 0.0770 grams AgBr.
Percentage found: Br 48.12
$C_4H_5O_2Br$. Calculated percentage: Br 48.48.

* The treatment of the mother liquor is described below under 2).

The calcium salt was obtained by the action of calcium carbonate on the acid. The crystals that precipitated after evaporation were filtered off, washed in ether and dried at 105°.

0.0701 grams of substance: 0.0257 grams $CaSO_4$.
Percentage found: Ca 10.78.
$(C_4H_4O_2Br)_2Ca$. Calculated percentage: Ca 10.87.

Laboratory of Organic Chemistry
of the Far-Eastern Branch of the Academy of Sciences
of the USSR and the Far-Eastern
State University.

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GEOLOGY

ON EXISTENCE OF UPPER TRIASSIC IN THE REGION OF BUREYA RIVER BASIN

By N. S. VORONETS

(Communicated by A. A. Borissiak, Member of the Academy. 17. II. 1937)

The Bureya Expedition of the All-Union Institute of Mineral Raw Materials under the leadership of A. K. Matveev has been conducting, since 1934, a systematical geological study of the deposits in the region of the Bureya River basin. In 1936, it investigated the district of the middle course of the River Tyrma, the left tributary of the Bureya River. Triassic deposits were found here. There is no need to emphasize the importance of this discovery, made amidst a great area covered, as was hitherto thought, by Jurassic marine deposits, the oldest of which were referred to the Middle Liassic([3]).

The fauna were collected from light brownish-gray calcareous sandstones and, unfortunately, in very limited numbers. They were delivered by N.P. Krasheninnikov to the author, who identified, in this small collection, *Spiriferina* sp. indet., *Halorella* sp. [ex. gr. *H. pedata* (Bronn.) Bittner [and *Halorella* sp.] ex gr. *H. amphitoma*(Bronn.) Bittner ([1])], which he refers to the Upper Triassic.

The fauna from other outcrops belong to forms already known to exist in the Middle and Upper Liassic of the Bureya River basin (l. c.) and consequently the author does not dwell upon them.

It should be mentioned that the genus *Halorella*, as is well known, was shown by A. Bittner ([1]) to belong to Alpine forms occurring only in the Upper Triassic.

A region related to the Bureya region in the sense of possessing similar Upper Triassic fauna, is the Kolyma Region. The *Brachiopoda* classified by A. Moisseev ([4]) consist of the following species: *Spiriferina* sp. indet., *Halorella* sp. indet., and others; the age of these deposits was established by L. Kiparisova ([5]) as being Karnian according to the *Lamellibranchiata*.

From what has preceded it is apparent that, being unable to define the age of the Tyrma fauna on account of the small size of the collection and the absence of key forms, we can only refer it, for the present, to the Upper Triassic.

From a palaeogeographic point of view, the presence in the Bureya region of Upper Triassic fauna in common with the Kolyma region is quite interest-

ing. It would seem that the Ussuri Gulf had a more extended area in the Upper Triassic, just as in the Jurassic, and reached westward into the basin of the Bureya river (2).

Central Geological Research
Institute Leningrad.

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GENETICS

THE THIRD VARIANT IN THE «TRIANGLE METHOD»

By A. S. SEREBROVSKY, Corresponding Member of the Academy

In making use of the «triangle method» ([1,2]) in the analysis of quantitative characters, a decisive factor is the accuracy with which we plot the empirical points in the M—σ^2 field. For small sibs, the dispersion due to the influence of random sampling and paratypical variability may prove so big as to render the «triangle» figure blurred and difficult to read. In our previous communication ([2]) we described a method of «joint sibs» which increased the number of members of each sibs as well as the accuracy of the empirical points in the field.

Fig. 1.

In the present communication, we describe a new variant of the triangle method based on the method of «joint-sibs». We group sibs resulting from the mating of one and the same male to several of his daughters, the latter issuing from one mother and so forming a group of full sisters. In the communication([2]), we noted the interesting advantages resulting from the mating of a father to his daughter (Fig. 1, *1*.) The present variant is an extension of this case to several daughters.

The mating of a father to two of his daughters (from one mother) gives ten possible types of monohybrid matings, as recorded in Table 1, types five and six giving joint sibs with one and the same characteristic $M=i$, $\sigma^2=\frac{1}{2}i^2$. In this way, the full drawing consists of nine theoretical points (forming a frame). In Table 1 appear the frequencies of different types of matings under the assumption that the population is a random one. In Fig. 1, *2* is shown a triangle of nine points, every point being represented by a group of dots corresponding to frequencies of each of the nine points of the frame,

Table 1

Types of father × 2 daughters matings

Parental matings ♂ × ♀	Frequencies	1 $aa\times aa$ $aa\times aa$ 0 0	2 $aa\times aa$ $aa\times Aa$ $\frac{1}{4}\,i\ \ \frac{3}{16}\,i^2$	3 $aa\times Aa$ $aa\times Aa$ $\frac{1}{2}\,i\ \ \frac{4}{16}\,i^2$	4 $Aa\times aa$ $Aa\times Aa$ $\frac{3}{4}\,i\ \ \frac{7}{16}\,i^2$	5 $Aa\times Aa$ $Aa\times Aa$ $i\ \ \frac{1}{2}\,i^2$	6 $Aa\times aa$ $Aa\times AA$ $i\ \ \frac{1}{2}\,i^2$	7 $Aa\times Aa$ $Aa\times AA$ $\frac{5}{4}\,i\ \ \frac{7}{16}\,i^2$	8 $Aa\times AA$ $Aa\times AA$ $\frac{6}{4}\,i\ \ \frac{1}{4}\,i^2$	9 $AA\times Aa$ $AA\times AA$ $\frac{7}{4}\,i\ \ \frac{3}{16}\,i^2$	10 $AA\times AA$ $AA\times AA$ $2i$ 0
$aa\times aa$	q^4	q^4	—	—	—	—	—	—	—	—	—
$aa\times Aa$	$2pq^3$	$\frac{1}{2}\,pq^3$	pq^3	$\frac{1}{2}\,pq^3$	—	—	—	—	—	—	—
$aa\times AA$	p^2q^2	—	—	p^2q^2	—	—	—	—	—	—	—
$Aa\times aa$	$2pq^3$	—	—	$\frac{1}{2}\,pq^3$	pq^3	$\frac{1}{2}\,pq^3$	—	—	—	—	—
$Aa\times Aa$	$4p^2q^2$	—	—	$\frac{1}{4}\,p^2q^2$	p^2q^2	p^2q^2	$\frac{1}{2}\,p^2q^2$	p^2q^2	$\frac{1}{4}\,p^2q^2$	—	—
$Aa\times AA$	$2p^3q$	—	—	—	—	$\frac{1}{3}\,p^3q$	—	p^3q	$\frac{1}{3}\,p^3q$	—	—
$AA\times aa$	p^2q^2	—	—	—	—	—	—	—	p^2q^2	—	—
$AA\times Aa$	$2p^3q$	—	—	—	—	—	—	—	$\frac{1}{2}\,p^3q$	p^3q	$\frac{1}{2}\,p^3q$
$AA\times AA$	p^4	—	—	—	—	—	—	—	—	—	p^4
Total . .	1	$\frac{q^3(q+1)}{2}$	pq^3	$pq^2\left(1+\frac{q}{4}\right)$	pq^2	$\frac{pq}{2}$	$\frac{p^2q^2}{2}$	p^2q	$p^2q\left(1+\frac{p}{4}\right)$	p^3q	$\frac{p^3(p+1)}{2}$
at $p=q=\frac{1}{2}$		$\frac{3}{32}$	$\frac{1}{16}$	$\frac{9}{64}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{32}$	$\frac{1}{8}$	$\frac{9}{64}$	$\frac{1}{16}$	$\frac{3}{32}$
Relative frequency		6	4	9	8	8	2	8	9	4	6
						10					

Table 2

Types of father×4 daughters matings

Parental matings ♂×♀	Frequencies	Frame points 1	2	3	4	5	6	7	8	9	10	etc $\frac{x}{2di}$ etc $\frac{y}{4d^2i^2}$
		$M=0$ $\sigma^2=0$	$\frac{1}{8}i$ $\frac{7}{64}i^2$	$\frac{2}{8}i$ $\frac{12}{64}i^2$	$\frac{3}{8}i$ $\frac{15}{64}i^2$	$\frac{4}{8}i$ $\frac{16}{64}i^2$	$\frac{5}{8}i$ $\frac{23}{64}i^2$	$\frac{6}{8}i$ $\frac{28}{64}i^2$	$\frac{7}{8}i$ $\frac{31}{64}i^2$	$\frac{8}{8}i$ $\frac{32}{64}i^2$	$\frac{9}{8}i$ $\frac{31}{64}i^2$	
$aa\times aa$	q^4	q^4	—	—	—	—	—	—	—	—	—	—
$aa\times Aa$	$2pq^3$	$\frac{1}{8}pq^3$	$\frac{4}{8}pq^3$	$\frac{6}{8}pq^3$	$\frac{4}{8}pq^3$	$\frac{1}{8}pq^3$	—	—	—	—	—	—
$aa\times AA$ . . .	p^2q^2	—	—	—	—	p^2q^2	—	—	—	—	—	—
$Aa\times aa$	$2pq^3$	—	—	—	—	$\frac{1}{8}pq^3$	$\frac{4}{8}pq^3$	$\frac{6}{8}pq^3$	$\frac{4}{8}pq^3$	$\frac{1}{8}pq^3$	—	—
$Aa\times Aa$ . . .	$4p^2q^2$	—	—	—	—	$\frac{1}{64}p^2q^2$	$\frac{8}{64}p^2q^2$	$\frac{28}{64}p^2q^2$	$\frac{56}{64}p^2q^2$	$\frac{70}{64}p^2q^2$	$\frac{56}{64}p^2q^2$	etc
$Aa\times AA$ . . .	$2p^3q$	—	—	—	—	—	—	—	—	$\frac{1}{8}p^3q$	$\frac{4}{8}p^3q$	etc
etc . .												
Relative frequency		4.5	2	3	2	5	2.5	5	5.5	5.5	5.5	

Points of the frame (1—13) and types

Parental matings	Frequencies	1	2	3	4	5	6	
		1	2	3	4	5	6	7
		$aa\times aa$ $\times aa$ $\times aa$	$aa\times aa$ $\times aa$ $\times Aa$	$aa\times aa$ $\times Aa$ $\times Aa$	$aa\times Aa$ $\times Aa$ $\times Aa$	$Aa\times aa$ $\times aa$ $\times Aa$	$Aa\times aa$ $\times Aa$ $\times Aa$	$Aa\times aa$ $\times Aa$ $\times AA$
$aa\times aa$ . .	q^4	q^4	—	—	—	—	—	—
$aa\times Aa$ . .	$2pq^3$	$\frac{1}{4}pq^3$	$\frac{3}{4}pq^3$	$\frac{3}{4}pq^3$	$\frac{1}{4}pq^3$	—	—	—
$aa\times AA$ . .	p^2q^2	—	—	—	p^2q^2	—	—	—
$Aa\times aa$ . .	$2pq^3$	—	—	—	$\frac{1}{4}pq^3$	$\frac{3}{4}pq^3$	$\frac{3}{4}pq^3$	—
							15	
$Aa\times Aa$ . .	$4p^2q^2$	—	—	—	$\frac{1}{16}p^2q^2$	$\frac{6}{16}p^2q^2$	$\frac{12}{16}p^2q^2$	$\frac{3}{16}p^2q^2$
$Aa\times AA$ . .	$2p^2q$	—	—	—	—	—	—	—
$AA\times aa$ . .	p^2q^2	—	—	—	—	—	—	—
$AA\times Aa$ . .	$2p^2q$	—	—	—	—	—	—	—
$AA\times AA$.	p^4	—	—	—	—	—	—	—
Total at $p=q=\frac{1}{2}$	—	$\frac{1}{64}+\frac{1}{64}$	$\frac{3}{64}$	$\frac{3}{64}$	$\frac{1}{64}$ $\frac{1}{16}$ $\frac{1}{64}$ $\frac{1}{256}$	$\frac{3}{64}$ $\frac{6}{256}$	$\frac{3}{64}$ $\frac{12}{256}$	$\frac{3}{256}$
Relative frequency at $p=q=\frac{1}{2}$		20	12	12	25	18	24	3
							27	
Number of points in fig. 1, *2* (4=1 point)		5	3	3	6	4	7	

assuming that $p=q=\frac{1}{2}$. Table 3 (*p.* 570—571) and Fig. 1, *3* are similarly constructed and refer to the case when there are three daughters. Sixteen types of matings are possible in this case. Of these, the sixth and seventh, eighth and ninth, tenth and eleventh give fused sibs with similar characteristics, which explains why we obtain a thirteen-point frame of triangle.

Table 2 (*p.* 569) and Fig. 1, *4* give a seventeen-point frame corresponding to the case of four daughters.

In this table, instead of the types of crosses, the points of the frame are given, since all the types of crosses having similar characteristics are summarized. In such a construction, it is easier to understand the laws governing the frequency of points. In the horizontal rows appear the binomial coefficients.

Fig. 1, *5* represents the case of five daughters.

It is not difficult to see the laws that govern changes in the frame of the triangle corresponding to an increase in the number of daughters. Each

Table 3.

of father ×3 daughters matings (1—16)

7		8		9	10	11	12	13
8	9	10	11	12	13	14	15	16
$Aa\times Aa$ $\times Aa$ $\times Aa$	$Aa\times aa$ $\times Aa$ $\times AA$	$Aa\times aa$ $\times AA$ $\times AA$	$Aa\times Aa$ $\times Aa$ $\times Aa$	$Aa\times Aa$ $\times AA$ $\times AA$	$Aa\times AA$ $\times AA$ $\times AA$	$AA\times Aa$ $\times Aa$ $\times AA$	$AA\times Aa$ $\times AA$ $\times AA$	$AA\times AA$ $\times AA$ $\times AA$
—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—
$\frac{1}{4}pq^3$	—	—	—	—	—	—	—	—
20		15						
$\frac{8}{16}p^2q^2$	$\frac{12}{16}p^2q^2$	$\frac{3}{16}p^2q^2$	$\frac{12}{16}p^2q^2$	$\frac{6}{16}p^2q^2$	$\frac{1}{16}p^2q^2$	—	—	—
$\frac{1}{4}p^3q$	—	—	$\frac{3}{4}p^3q$	$\frac{3}{4}p^3q$	$\frac{1}{4}p^3q$	—	—	—
—	—	—	—	—	p^2q^2	—	—	—
—	—	—	—	—	$\frac{1}{4}p^3q$	$\frac{3}{4}p^3q$	$\frac{3}{4}p^3q$	$\frac{1}{4}p^3q$
—	—	—	—	—	—	—	—	p^4
$\frac{1}{64}$ $\frac{8}{256}$	$\frac{12}{256}$	$\frac{3}{256}$	$\frac{12}{256}$ $\frac{3}{64}$	$\frac{6}{256}$ $\frac{3}{64}$	$\frac{1}{256}$ $\frac{1}{64}$	$\frac{3}{64}$	$\frac{3}{64}$	$\frac{1}{64}+\frac{1}{16}$
$\frac{1}{64}$					$\frac{1}{16}+\frac{1}{64}$			
16	12	3	24	18	25	12	12	20
28		27						
7				4	6	3	3	5

additional daughter adds four points to the frame (one daughter=5 points, two daughters=9 points, etc.). Of all these points, five are unchanged and remain in the same place as in the case when there is one daughter. (1) 0,0; (2) $\frac{1}{2}$, $\frac{1}{4}$; (3) 1, $\frac{2}{4}$; (4) $\frac{3}{2}$, $\frac{1}{4}$, and (5) 2,0. But to these five original points new ones are added. An increase in the number of daughters results in a corresponding increase in the number of these points. They are distributed along parabolic lines passing through the principal points. On axis M, the distance between the points is equal to $\frac{i}{2d}$, where i denotes the force of gene influence and d the number of daughters. On axis σ^2, the intervals between the points on all the four parabolic segments correspond to a series of the differences of squares of the neighbouring natural numbers. Because of this, the additional points are closer together on the right, this being the better expressed the more daughters there are. When there is an infinite

number of daughters, we have again five points just as when there is one daughter, but with some differences in the corresponding frequencies (Fig. 1, *6*).

1
3
8
3
1

What is important for our present purposes is that the structure of the monohybrid triangle is simpler and, more especially, that the diagram resembles open compasses resting its legs upon the M axis with an interval between the legs equal to $2i$. Moreover, the frequency of these two extreme points is sufficiently high and changes from 12.5% when there is one daughter (both points together giving 25%) to 6.25 % for an infinite number of daughters (both points together giving 12.5%).

The accuracy of the empirical points in cases when there are four daughters increases twofold; in cases of nine daughters, threefold. Thus, we are able to discover and study genes which are two and three times weaker in their influence. Since the distance between the points is $2i$ as against i in a simple monohybrid triangle, the results are again twice as accurate.

The following modification of the method is possible. In order to increase the number of joint sibs, it is possible to join sibs from matings between fathers and daughters to sibs issuing from matings between father and mother, where the latter is the mother of daughters who were mated to their father. In cases of two daughters, this operation increases the number of joint sibs by one third; when there are three daughters, by one fourth. The drawing of the monohybrid frame (father × mother)+(father × daughter) will resemble the frame (father × two daughters). The frame (father × mother)+(father × × two daughters) will resemble the frame (father × three daughters), i. e., the mother may be approximately put equal to one daughter. In such cases, however, two additional points arise in the monohybrid frame when $M = \frac{4}{6}\, i$ and $\sigma^2 = \frac{8}{36}\, i^2$ (for the case of two daughters and a mother) and, symmetrically when $M = \frac{8}{6}\, i$ and $\sigma^2 = \frac{8}{36}\, i^2$ both with a frequency p^2q^2. The first of these corresponds to the mating $aa \times (Aa+Aa+AA)$ and the second to the mating $AA \times (Aa+Aa+aa)$; such types in crosses between father and daughter are obviously impossible.

Fig. 2 represents the frame for the case of two daughters + mother. A comparison of Fig. 2 with Fig. 1, *2* and 1, *3* shows a marked similarity of the former with Fig. 1, *3*, yet displaying the above-mentioned slight difference. In cases when there are numerous daughters, the difference will be still slighter, although, in this case, the addition of maternal sibs will result in a smaller increase of accuracy.

Fig. 2.

Laboratory of Genetics.
University of Moscow.

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GENETICS

ON THE INHERITANCE OF BIOCHEMICAL CHARACTERS BY ANIMALS AND ITS RELATION TO THEIR GROWTH

I. Glutathion Concentration in the Blood and Difference in Size of Breeds of Farm Animals

By V. I. PATRUŠEV

(Communicated by A. A. Sapehin, Member of the Ukrainian Academy, 7. II. 1937)

The problem of animal growth is one of the most important, economically, yet one the genetics of which has not been sufficiently studied. Acquirement of control over the processes by which size is inherited is an especially urgent task confronting biology.

It has been shown that rabbit breeds of different sizes (Polish and Flanders) have a different rate of growth even in the early stages of the division of the fertilized ovum ([12,20])

It has also been shown that difference in growth rate is due to heredity. However, the mechanism of the action of the hereditary substance remains here, as also in most other genetical investigations, obscure, although it is in just this direction that mastery over the processes of the inheritance of growth is most likely to be found.

It is shown in biological literature that growth may be stimulated by many biochemical factors. Among these is glutathion, an intracellular substance present in all the organic tissues, especially in the growing ones ([1, 13, 14, 15, 19]).

Glutathion is a tripeptide of glutaminic acid, cystein and glycine. It was discovered in 1921 by Hopkins in beer yeast and was not long ago synthetized ([4, 5, 13]).

A number of investigators have studied the relation of glutathion to the growth of animals and have shown that its concentration in the tissues of embryos is correlated with the final size of breeds in rabbits and chickens. The larger the final weight and size of the breed, the higher is the concentration of glutathion in the tissues of the embryos ([2,6–11]).

It was against such a background that we began our investigation of biochemical characters in animals in connection with differences in growth, due to heredity.

The establishment of biochemical differences between breeds of farm animals having different sizes and productiveness, the study of the possibilities of making use of biochemical characters in aminal breeding and

the investigation of their genetical causes—such is the sum and substance of the problems we undertook in this study. We began with a study of the intensity of the oxidation—reduction processes in tissues, because these processes are intimately connected with synthesis of proteins and therefore, from our point of view, must probably have a material connection with growth. Glutathion and catalase (see our second paper), previously studied by other investigators, were chosen as indices of the oxidation—reduction processes.

Concentrations of glutathion were determined in the blood of young and adult animals but not in the tissues of embryos, as was done by the authors above cited. The reason for choosing this method was the desire to utilize glutathion as a selectional character in case the investigation gave positive results.

In the summer of 1936, the concentration of glutathion in the blood of horned cattle and sheep was studied. The following cattle were subjected to investgation: the cattle of Daghestan highlanders, the Kalmyk cattle and their crosses with Aberdeen-Angus, Shorthorns, Herefords and also the thoroughbred Shorthorns and Herefords of the Salsk Zootechnical Station of the People's Commissariat of State Farms. This series of breeds embraces the extremes of size in the animals, beginning with the small highlanders' cattle, of an average weight of 160 to 170 kg, and ending with the largest breed, the Herefords, weighing up to 1000 kg and over ([16–18]).

Among the sheep, the following were studied: Wurtembergs having an average weight of 66 kg, Gunib (highlanders') fat tails, live weight about 35 kg, and the cross from these two breeds([3]). The sheep belonged to the state farm «Chokh», Daghestan Autonomous Soviet Socialist Republic.

The blood was taken from the left jugular, mornings after milking, before driving the animals to pasture. The determinations of glutathion were made by Woodward and Fry's method ([4]).

The experiments showed that the concentration of glutathion in the blood of horned cattle decreases with age, beginning from the third or fourth year. Pregnancy influences concentration of glutathion: the concentration increases as the parturition draws nearer ($r=0.46\pm0.09$; $n=65$).

It was shown that in rapidly growing calves owing to their more copious feeding, the concentration of glutathion is higher than in less vigorously growing calves (the error of difference is 3.8 times less than the difference of the average indices; $n=89$). Determinations of glutathion made in the same animals at different times did not always coincide. The average difference in the determinations was 5 to 6 per cent.

Even during the course of the day, the glutathion content is not identical. In the morning, before feeding and watering, the glutathion content is usually higher. After midday watering, the concentration falls about 10 or 15 per cent, while toward evening there is a sligth rise.

Differences in the glutathion content in the blood of different breeds are shown in Tables 1 and 2.

The highest concentration of glutathion is characteristic of the Kalmyk cattle, the Herefords and their crosses. Then come the Shorthorns, and their crosses with the Kalmyk cattle, then, the crosses with the Aberdeen-Angus. The highlanders'cattle are in the last place.

Among the sheep, the Wurtembergs had the highest concentration of glutathion; the Gunib sheep, the lowest. Crosses between these had a medium concentration (nearer to the indices of the highlanders' sheep).

Thus, differences in glutathion content in the different breeds are statistically significant. On this ground, we consider concentration of glutathion

Table 1

Differences in the Concentration of Glutathion in the Blood of Different Breeds of Sheep

No	Breed	n	m	$\pm m$	σ	$\pm m$	C	lim
1	Wurtemberg	18	33.44	1.8	7.8	1.3	22.7	19—48
2	F_b Wurtemberg . . .	11	31.9	3.4	11.6	2.6	36.4	15—49
3	F_2	13	28.4	3.2	11.2	2.2	39.8	13—47
4	F_1 Wurtemberg × Gunib	13	23.8	2.8	10.4	2.08	44	3—93
5	Gunib	21	25.3	2.8	12.8	1.9	50.6	11—40

Table 2

Differences in the Concentration of Glutathion in the Blood of Different Breeds of Horned Cattle

No	Breed	n	M	$\pm m$	σ	$\pm m$	C	lim	Remarks
	I. Calves born in 1936								
1	Kalmyk cattle . . .	92	37.02	0.62	5.9	0.43	15.9	24—57	Calves of both sexes investigated at the age of 1 to 2 months in August, 1936
2	F_1 Shorthorn × Kalmyk	99	30.59	0.31	3.14	0.22	10.2	22—40	
3	F_b Shorthorn × Kalmyk (F_1 × Shorthorn)	12	29.5	1.08	3.76	0.76	12.7	26—38	
4	F_1 Aberdeen-Angus × Kalmyk . .	30	32.2	0.83	4.56	0.58	14.1	20—44	
5	F_b Aberdeen-Angus × Kalmyk (F_1 × × Aberdeen-Angus)	21	25.67	0.88	4.04	0.62	15.70	16—36	
	II. First calves of 1933								
1	Kalmyk cattle . . .	87	38.0	0.51	4.78	0.36	12.5	26—50	Investigation conducted in August, 1936
2	F_1 Shorthorn × Kalmyk	88	32.08	0.81	7.6	0.57	23.6	20—46	
3	F_1 Aberdeen-Angus × Kalmyk . .	116	27.82	0.39	4.30	0.28	15.4	16—44	
	III. Horned Cattle older than 3 years								
1	Kalmyk cows . . .	85	36.71	0.54	5.08	0.38	13.8	22—50	Investigation conducted in August, 1936
2	» » . . .	84	37,73	0.64	5.88	0.48	15.5	26—50	
3	Storthorn breeders .	6	32.3	1.72	4.20	1.21	12.9	25—41	
4	Shorthorn + thoroughbred cows	46	31.3	1.15	7.86	0.81	25.1	16—40	Investigation conducted in June, 1936
5	F_1 Kalmyk × Shorthorns	19	29.52	2.55	11.1	1.8	37.6	14—45	
6	Herefords	14	37.0	2.09	7.81	1.47	21.1	20—50	
7	F_1 Kalmyk × Herefords	24	38.4	1.67	8.16	1.17	21.2	24—52	
8	Highlanders'cattle .	33	21.12	0.94	5.4	0.66	25.5	6—34	Investigated May, 1936

a hereditary character. The glutathion content in half-bloods of the first generation, which approximates that of the parent breed having the smaller concentration, also points to this fact. The results of our investigation give ground for considering the low glutathion content as dominant in the first generation of crosses between breeds.

The decrease of glutathion content from breed to breed corresponds to the decrease in size and weight of the breeds. This holds for both cattle and sheep.

The Kalmyk cattle, having one of the highest concentrations of glutathion but lighter in weight than the Shorthorns, Aberdeen-Angus and the crosses of the latter with Kalmyk cattle are an exception.

This peculiarity of Kalmyk cattle may, in our opinion be explained by their more lively temperament and, consequently, their more intensive rate of metabolism as compared with the cattle of the other breeds investigated.

A comparison of the concentration of glutathion and of the live weight in groups of animals of the same strains is given in Table 3.

Table 3

Comparison of the Concentration of Glutathion in the Blood and of the Live Weight of Groups of Animals of the Same Strains

No	Designation of group	Concentration of glutathion in milligram %	Number of animals	Average live weight in kg	Remarks
1	Kalmyk calves of the Kirnov herd at birth	> 40	8	24.1	Live weight at birth
		30—40	48	22.8	
		< 30	10	20.0	
2	F_1 Aberdeen-Angus × Kalmyk calves at birth	> 34	4	28.7	Live weight at birth
		29—34	8	28.1	
		< 29	5	27.4	
3	F_1 Shorthorn × Kalmyk	> 31	13	28.6	Live weight at birth
		< 31	16	27.7	
4	Kalmyk cows older than 3 years	> 40	15	480.2	Live weight at time of investigation
		30—40	57	472.0	
		< 30	10	445.5	
5	F_1 Shorthorn × Kalmyk older than 3 years	> 35	28	445	Live weight at time of investigation
		29—35	27	418.9	
		< 29	24	417.0	

It is apparent from the table that in all the groups the animals having a high glutathion content have also a high average live weight.

On the basis of these data, we come to the following conclusions:

1. Breeds of horned cattle and of sheep which differ in their final sizes, live weights and rates of attaining maturity manifest regular differences in the glutathion content of their blood.

2. Within groups of the same strain, the animals that have a higher glutathion content in their blood, are, as a rule, of larger size and heavier.

3. Further study of the variability and hereditability of glutathion concentration in the blood is needed before this character can be recommended for extensive introduction into selectional work with animals.

Institute of Genetics.
Academy of Sciences of the USSR.
Moscow.

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ON THE INHERITANCE OF BIOCHEMICAL CHARACTERS BY ANIMALS AND ITS RELATION TO THEIR GROWTH

II. The Catalase Content in the Blood of Horned Cattle and of Sheep

By V. I. PATRUŠEV

(Communicated by A. A. Sapehin, Member of the Ukrainian Academy, 7. II. 1937)

The growth of animals is connected with the oxidation—reduction processes in the body cells as aspects of the synthesis of protein. On that account, the investigation of the oxidation—reduction processes in the body cells of different breeds of animals in connection with their growth ought to prove quite timely.

We decided to investigate the catalase content in the blood as being one of the indices of the oxidation—reduction processes. This choice was determined partly by the fact that difference in catalase content has been studied from a genetical viewpoint in guinea pigs, chickens, horned cattle and sheep and that these studies have established its hereditary character ([1, 3, 4, 6, 8, 9.]). This considerably lightened our task. It was necessary only to compare the activity of the catalase of the blood of breeds differing from each other in size.

The investigation was carried out on the same breeds of horned cattle and sheep as were designated in the author's first paper on this subject. Analyses for catalase were made at the same time as the analyses for glutathion.

Academician Bach's method was used for the determination of catalase.

A preliminary test of the suitability of this method for determining catalase in genetical investigations showed that, just as in the case of glutathion, the great variability of catalase under the influence of various factors has to be kept in mind.

Determinations of catalase made on the same animals on different days show great divergences in results (up to 20 or 30 per cent).

There is a still greater *divergence with respect to time of day* (Table 1). *In the case of all animals, the determinations showed the highest catalase content in the morning; toward midday and evening, there occurrs a gradual drop in catalase content.*

Variability due to differences in age also cannot be neglected. Catalase content proved to be considerably higher in calves than in adult animals (Table 2).

Desiring to eliminate all these factors, we strove for uniformity of all the conditions that might influence the results of the analyses. Investigations

were limited to healthy animals only. The blood was taken in the morning before feeding the animals or driving them to pasture. Only groups, all members of which were of a similar age, were selected for comparisons.

Table 1

Daily Variation of the Catalase Content in Calves and Cows

Catalase content	Calves			Cows		
	Morning	Noon	Evening	Morning	Noon	Evening
2—2.2	—	—	—	—	—	1
2.2—2.4	—	—	—	—	—	—
2.4—2.6	—	—	—	—	—	—
2.6—2.8	—	—	—	—	—	2
2.8—3.0	—	—	—	—	—	—
3.0—3.2	—	—	—	1	—	1
3.2—3.4	—	—	2	—	—	1
3.4—3.6	—	—	—	—	—	2
3.6—3.8	—	1	—		—	—
3.8—4.0	—	—	2	—	1	2
4.0—4.2	—	2	—	1	1	—
4.2—4.4	—	2	—	—	—	1
4.4—4.6	1	—	1	2	1	—
4.6—4.8	1	1	1	—	1	—
4.8—5.0	2	—	1	—	—	—
5.0—5.2	—	3	1	-	2	—
5.2—5.4	1	—	—	—	1	—
5.4—5.6	—	—	—	—	—	—
5.6—5.8	—	1	1	3	1	—
5.8—6.0	1	—	—	—	1	—
6.0—6.2	1	—	—	1	—	—
6.2—6.4	1	—	—	—	—	—
6.4—6.6	—	—	—	—	—	—
6.6—6.8	—	—	—	1	—	—
6.8—7.0	—	—	-	—	1	-
7.0—7.2	1	—	—	1	—	-
7.2—7.4	—	—	—	—	-	-
7.4—7.6	1	—	—	—	—	—
	10	10	9	10	10	10
	5.78	4.62	4.36	5.32	5.12	3.5
	±0.3	±0.1	±0.2	±0.3	±0.2	±0.2

The investigation of difference in catalase content according to breeds established the fact that *catalase activity changes from breed to breed in just the same order as was noted in the case of glutathion.* The Kalmyk cattle have the highest catalase content. We note in passing that Putilina published analogous data for Kalmyk cattle(5). Then come the half-bloods of Kalmyk cattle with Shorthorns and Aberdeen-Angus. Redpole-Kalmyk cattle stood in the last place (Table 2).

The figures everywhere show the amount of catalase in 1 cm^3 of blood.

In view of the inconsiderable number of pure-blood animals investigated, we do not include the results of those in the table. On the grounds of the 6 to 10 analyses for each of the pure-blood groups of animals, we may conclude that the Shorthorns and Aberdeen-Angus have the same or lower catalase content as their half-bloods with the Kalmyk cattle. These data give

grounds for supposing the low catalase content to be dominant. This deduction, however, requires special experimental confirmation.

Table 2

Difference Between Breeds of Horned Cattle in Respect to Catalase Content

Serial №	Groups of animals	n	M	$\pm m$	σ	$\pm m$	C	lim
1	Kalmyk calves born in 1936	91	5.32	0.11	1.06	0.07	20	2.2—7.8
2	Ditto	44	5.63	0.17	1.18	0.12	20.9	2.2—7.8
3	Ditto	10	5.4	0.39	1.23	0.27	22.8	2.3—6.7
4	F_1 Aberdeen-Kalmyks born in 1936	31	3.64	0.18	1.0	0.12	27.5	1.0—5.8
5	F_b Aberdeen-Kalmyks born in 1936 ($F_1 \times$ Aberdeen)	22	2.56	0.09	0.43	0.06	16.8	1.8—3.6
6	Kalmyk cows born in 1933	83	4.53	0.1	0.92	0.07	20.3	1.8—7.4
7	F_1 Shorthorn-Kalmyks, 1933	76	3.76	0.05	0.5	0.04	13.3	2.4—5.4
8	F_1 Aberdeen-Kalmyks, 1933	112	2.86	0.05	0.55	0.03	19.3	1.2—4.4
9	F_1 Redpole-Kalmyks, 1934	21	2.56	0.19	0.89	0.13	35.08	1.0—4.4
10	Kalmyk cows more than 3 years old	85	4.56	0.11	1.03	0.07	22.5	1.4—7.0
11	Ditto	84	4.75	0.1	0.94	0.07	19.9	2.2—7.2

The parallelism of change of catalase and glutathion content in the blood of the breeds of animals investigated is confirmed by the presence of a positive correlation between them. The corresponding figures are: for the herd of half-breeds of Aberdeen-Angus—Kalmyks of the first generation, $r = 0.32 \pm \pm 0.07$; for the herd of Shorthorn—Kalmyks, $r = 0.469 \pm 0.09$, etc. This correlation may be explained physiologically. The peroxides that form as a result of the action of glutathion are decomposed by catalase ([5]). As a result, the contents of glutathion and of catalase, being in a certain antagonism, are interrelated. When the one substance increases, the other does also.

The difference in catalase content between the different groups is mathematically real, when the average values are compared; however, the transgression with respect to this character is considerable.

On the basis of the differences with respect to catalase content established for different breeds, it may be concluded that *breeds of animals of energetic temperament have higher catalase content than phlegmatic, sluggish animals* (for example compare Kalmyk cattle with Shorthorns).

Among breeds of similar temperament, the highest catalase content is found in those groups that have the highest growth rate (for example, compare Shorthorns, Aberdeen-Angus and Redpoles).

Within one and the same breed, the animals having high catalase content have, on the average, greater weights than the animals with lower catalase content. This tendency can be seen from the following data (Table 3).

The existence of differences between breeds in regard to catalase content supports the view of its hereditary nature. Differences in the catalase content within breeds were established by the investigators mentioned above in the form of well isolated groups. This is likewise shown by our curves of the distribution of horned cattle and sheep within the breeds in respect of catalase content (see curves). These curves, in all cases, have 3, 4 or 5 peaks. In a number of cases, the ratios between the number of animals in the groups

Table 3

Correlation of the Catalase Content and of Live Weight within Groups of Animals of the Same Breed

Serial №	Groups of animals	Catalase content	Number of animals	Average live weight
1	Kalmyk calves at birth	>6	22	23.3
		4—6	58	22.9
		<4	5	21.2
2	The same at age of 1 month	>6	15	48.8
		4.5—6	10	46.4
		<4.5	7	45.8
3	Primapari Kalmyk cow, 3-year olds (from the Kirnov herd)	>5	36	386.0
		3.5—5.0	28	371.3
		<3.5	18	364.7
4	Primapari F_1 Shorthorn-Kalmyk cows, 3-year olds	>4	21	448
		3.5—4	21	442.7
		<3.5	25	435.7

formed by the curves reminds one of the picture of dihybrid splitting, as for example, 102 : 25 : 40 : 8 in the case of Kalmyk cows; 63 : 30 : 30 : 9, in the case of Kalmyk calves.

It must be noted that the distribution and calculation of animals by groups is somewhat artificial owing to the existence of a large transgression.

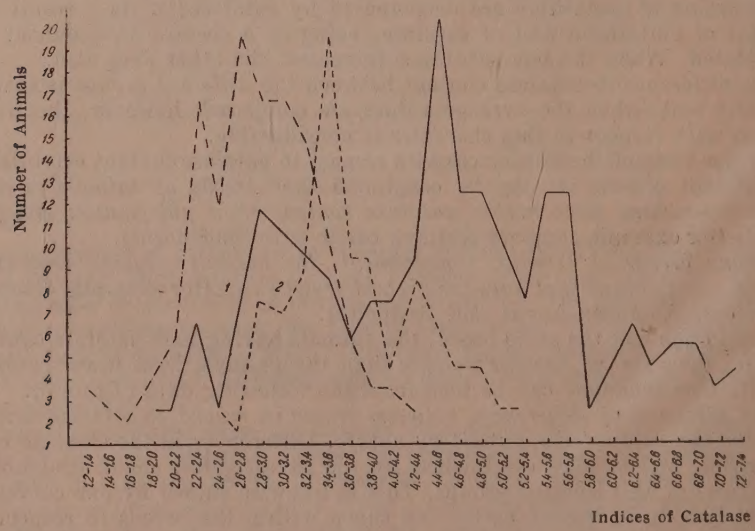

Fig. 1. Curves of Catalase Content in the Blood of Horned Cattle; *1*—Kalmyk calves, *2*—Shorthorn × Kalmyks, *3*—Aberdeen-Angus × Kalmyks.

Besides, the most numerous group of animals, in all cases, falls into two subgroups. Because of all this, we do not consider it possible to make any conclusion about the dihybrid nature of the inheritance of catalase, as some authors have done. Only direct experimentation can solve this problem.

In order to prove the hereditability of differences in catalase content, we made a general evaluation of the genotype of 30 breeders by comparing

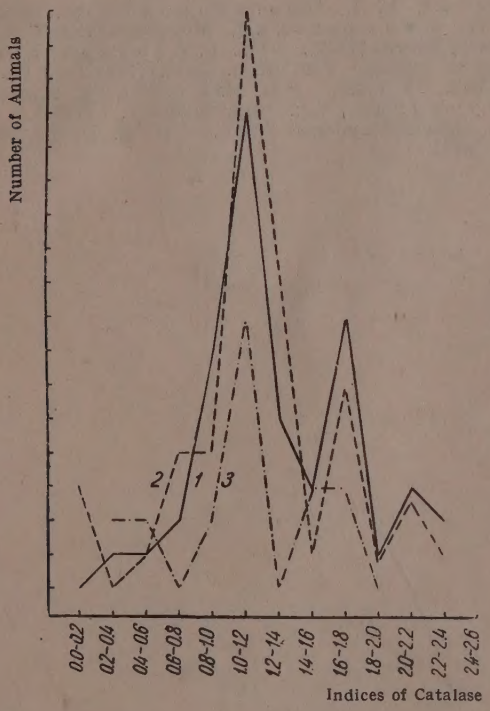

Fig. 2. Curves of Calatase Content in the Blood of Sheeps: *1*—Wurtembergs, *2*—$F_b \times$ Wurtemberg, *3*—F_1 Wurtemberg $\times$ Gunib.

the average catalase content of their offspring. The number of thelatter for each bull varied from 10 to 16 head. Comparison showed that, while the data for the majority of the breeders were similar, great deviations in the catalase content were to be observed in the offspring of certain bulls.

It is significant that Aberdeen-Angus bull No. 10, whom we had earlier differentiated as an «improver» in respect to glutathion, proved also to be an «improver» in respect to catalase—that is, his offspring had higher catalase content than that of other bulls.

On comparing the data on Wurtembergs, Gunib (mountain) sheep and crosses between the two, the differences in sheep with respect to catalase content proved to be unreal. Altogether 200 sheep were tested.

Thus, as a result of this work, *the fact of the inheritance of catalase content receives confirmation.* Besides, it is established *that the calatase content is correlated with temperament and with the body sizes of breeds.*

Institute of Genetics
Academy of Sciences of the USSR.
Moscow.

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